1994 ANNUAL REPORT
AND
FIVE-YEAR (1994-1998)
STRATEGIC INVESTMENT PLAN

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Strategic Environmental Research
and Development Program

A Partnership to Improve the Environment

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DoD EPA DOE

SERDP

Strategic Environmental Research and Development Program

A Partnership to Improve the Environment

This document was prepared for the Executive Director, Strategic Environmental Research and Development Program (SERDP) by

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FOREWORD

The Strategic Environmental Research And Development Program (SERDP) is mandated in 10 U.S.C. §§2091-2904. SERDP addresses environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DOE). It is conducted as a tri-agency program jointly managed by the DoD, DOE and Environmental Protection Agency (EPA) with participation by other Federal agencies including the National Oceanic and Atmospheric Administration (NOAA) and the National Aeronautics and Space Administration (NASA).

This report includes information required by 10 U.S.C. §2902 for the annual report to Congress. It includes allocated funding for Fiscal Years 1993 and 1994. The individual research projects were reviewed and selected by the SERDP Council in response to specific requirements for research and development. Prior to funding, all projects valued greater than or equal to $1,000,000 were reviewed and recommended by the SERDP Scientific Advisory Board (SAB). Their comments on each project can be found in the *SERDP Scientific Advisory Board FY 1992 Annual Report* and *SERDP Scientific Advisory Board FY 1993 Annual Report*, both of which have been forwarded to Congress from the Chairman of the SAB via the Chair of the SERDP Council.

The SERDP *Strategic Investment Plan Fiscal Year 1993*, distributed to Congress in September 1993, was prepared based on a funding target of $180 million. The *SERDP Five-Year (1994-1998) Strategic Investment Plan* (Appendix A) is based on a FY 1994 appropriation of $160 million and is submitted on behalf of the SERDP Council whose membership consists of: the Director of Defense Research and Engineering; the Deputy Under Secretary of Defense (Environmental Security); the Vice Chairman of the Joint Chiefs of Staff and representatives from each of the uniformed Services and Coast Guard; the Assistant Secretary of the Air Force, Space; the Director of the DOE Office of Energy Research; the Assistant Secretary of Energy for Environmental Restoration and Waste Management; the Assistant Secretary of Energy for Defense Programs; and the Administrator of the EPA.

ACRONYMS

Each acronym used in the text is defined in its first use. This section provides a summary list of all acronyms.

A	Army
AF	U.S. Air Force
ARPA	Advanced Research Projects Agency
CIA	Central Intelligence Agency
CRADA	Cooperative Research and Development Agreement
DNA	Defense Nuclear Agency
DoD	Department of Defense
DOE	Department of Energy
DOI	Department of the Interior
DOIT	Develop On-Site Innovative Technologies
DSPO	Defense Support Program Office
EPA	Environmental Protection Agency
EQ Strat Plan	Environmental Quality Strategic Research and Development
ETF	Environmental Task Force
GOCO	Government-Operated, Government-Owned/Contractor-Operated
HAZMIN	Hazardous Waste Minimization
IPPD	Integrated Product/Process Development
LOVA	Low Vulnerability Ammunition
N	U.S. Navy
NASA	National Aeronautics and Space Administration
NETDP	National DoD Environmental Technology Demonstration Program
NOAA	National Oceanic and Atmospheric Administration
PEP	Propellants, Explosives, Pyrotechnics
POL	Petroleum, Oil, Lubricants
R&D	Research and Development
SAB	Scientific Advisory Board
SERDP	Strategic Environmental Research and Development Program
TTAWG	Technology Thrust Area Working Group
USDA	United States Department of Agriculture
USGCRP	U.S. Global Change Research Program
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound

INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) is mandated in 10 U.S.C. §§2901-2904. SERDP addresses environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DOE). According to this law, the purposes of the Program are:

(1) To address environmental matters of concern to DoD and the DOE through support for basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.

(2) To identify research, technologies, and other information developed by the DoD and the DOE for national defense purposes that would be useful to governmental and private organizations involved in the development of energy technologies and of technologies to address environmental restoration, waste minimization, hazardous waste substitution, and other environmental concerns, and to share such research, technologies, and other information with such governmental and private organizations.

(3) To furnish other governmental organizations and private organizations with data, enhanced data collection capabilities, and enhanced analytical capabilities for use by such organizations in the conduct of environmental research, including research concerning global environmental change.

(4) To identify technologies developed by the private sector that are useful for DoD and DOE defense activities concerning environmental restoration, hazardous and solid waste minimization, and prevention, hazardous material substitution, and provide for the use of such technologies in the conduct of such activities.

SERDP identifies and develops technology to enhance capabilities to meet environmental commitments and to foster the exchange of scientific information and technologies among the participants, other governmental agencies, and the private sector. The SERDP leverages and interacts with other environmental programs to identify and solve defense specific needs, extends applications of defense information to others, and builds on existing science and technology to derive more useable and cost-effective approaches for achieving reductions in environmental risks.

Description of Report

This is the first official annual report generated by SERDP, and it contains information since the Program's inception. FY 1991 and FY 1992 information is summarized in the October 1993 *Interim Status Report of the Council.* Project descriptions for FY 1991, 1992, and 1993 program years may be found in the Phase I, Phase II, and the Fiscal Year 1993 Strategic Investment Plan, respectively.

This annual report describes the progress made to date, as well as specific plans for the near-term to address the goals of SERDP. The combined efforts of the DoD, DOE, and EPA have been guided by the SERDP Council to assure that the SERDP is aggressively implemented. The efforts to date suggest there are multiple opportunities for synergistically exploiting and transferring environmentally related technologies developed by the agencies to each other, and to other government and private organizations. The *SERDP Five-Year (1994-1998) Strategic Investment Plan* (Appendix A) describes the Program's initial steps to fully integrate these multi-agency efforts.

The remainder of this report contains the following:

- Program Summary - major changes from the 1993 Interim Report are discussed, including the changes in number and emphasis of technology thrust areas. It also highlights significant achievements of the Program and changes in approach to program development from 1993 to 1994.

- Legislative Reporting Requirements - embodied within this report are the reporting requirements called for in 10 U.S.C. Section §2902(h)(2). Specifically addressed are:

  - actions to be taken during the five-year period covered by the plan to prevent duplication of research and development activities;

  - involvement with Federal Interagency coordinating entities, such as the Federal Coordinating Council of Science, Engineering, and Technology;

  - each project selected or recommended by the Council for support and funding, including the duration of, and the total estimated or actual cost (if known) of (i) each such project supported during the fiscal year in which the plan is submitted and the preceding fiscal year; and, (ii) each such project proposed for funding during the fiscal year in which the annual report is submitted and the following four fiscal years;

  - amounts made available for FY 1993 and FY 1994 to each Federal laboratory;

- amounts requested for SERDP for FY 1995;

- description of any changes in military specifications recommended by the Council, actions to be taken to effectuate and such recommended changes on an expedited basis, and the projected date for each such change;

- description of all contracts, agreements, or other documents for cooperative research and development activities entered into pursuant to the Stevenson-Wydler Technology Innovation Act of 1980 during FY 1993 and FY 1994;

- plans for transferring technology and information to other governmental agencies and to nongovernmental organizations involved in environmental research and related matters;

- description of plans to increase access by Federal government personnel, State and local government personnel, college and university personnel, industry personnel, and the general public to data under the control of, or otherwise available to, the DoD, relevant to environmental matters; and

- additional recommendations or proposals, including proposals for legislation, relating to the Strategic Environmental Research and Development Program as the Council considers appropriate.

• Appendix - contains the *SERDP Five-Year (1994-1998) Strategic Investment Plan,* which describes the Department's investment in SERDP over the next five years.

PROGRAM SUMMARY

The Strategic Environmental Research and Development Program is the Department's premier technology development and transfer mechanism for environmental issues. It fully leverages the complementary programs found within the uniformed Services, and those of DOE and EPA. The multi-agency management aspects of the Program have presented and continue to present significant challenges; however, the progress to date has also been substantial. The SERDP Council has collectively implemented a policy that takes full advantage of the inherent capabilities of the participating organizations and has directed the development of the Program which is fully compliant with the desires of the SERDP authorizing language.

The FY 1993 and FY 1994 SERDP efforts continued to emphasize the following objectives:

- To promote the maximum exchange of information, and to minimize duplication regarding environmentally related research, development and demonstration activities;

- To ensure that research and development activities under the SERDP do not duplicate other ongoing activities;

- To provide for appropriate access to data under the control of, or otherwise available to, DoD and DOE that is relevant to environmental matters;

- To provide governmental and nongovernmental entities with analytical assistance to address significant national and international environmental problems, including global environmental change research;

- To provide for the identification of energy technologies developed for national defense purposes that might have environmentally sound, energy efficient applications;

- To provide for the identification and support of programs of basic and applied research, development, and demonstration in technologies useful

    - to facilitate environmental compliance, remediation, and restoration activities;

    - to minimize waste generation, including reduction at the source;

    - to substitute use of nonhazardous, nontoxic, nonpolluting, and other environmentally sound materials and substances;

- To provide for the identification and support of research, development and application of other technologies developed for national defense purposes;

- To conduct joint research, development, and demonstration projects relating to innovative technologies, management practices and other approaches; and

- To provide for the identification of, and planning for the demonstration and use of, existing environmentally sound, energy-efficient technologies developed by the private sector.

FY 1993 PROGRAM

Overview

In FY 1993, several new initiatives commenced that enhanced our ability to successfully address Program objectives. SERDP expanded its technical focus from three major environmental R&D categories (Remote Sensing, Installation Restoration/Waste Management, and Energy) and identified six technology thrust areas. These were:

- Installation Restoration;
- Compliance;
- Conservation;
- Alternate/Clean Energy;
- Global Environmental Change; and
- Pollution Prevention.

Installation Restoration

This area focused on technology development and demonstration for more efficient, effective environmental cleanup of soil, sediment, groundwater, surface water and structures contaminated with hazardous, radioactive and toxic materials from past activities. Cleanup/remediation techniques, treatment technologies and monitoring assessment methods were the principal focus of this area.

Compliance

Compliance included technologies for environmental monitoring, waste treatment, end-of-pipe recycling and disposal, and environmental management not directly related

to site restoration, but related to meeting current and future environmental compliance requirements. It included understanding the fate and transport of defense related wastes and pollutants as well as methods and techniques for mitigating ecological and health impacts of these materials in the environment.

Conservation

This area is focused on research toward understanding, protecting, and maintaining biophysical resources and facilities relative to natural and cultural resources in order to ensure: (1) compliance with environmental laws; (2) sustained use of land and coastal resources; and (3) support for stewardship of those resources on relevant Federal lands. Those resources include all biophysical resources associated with and related to ecosystems and habitat, e.g., soils, vegetation, landform, water and biodiversity; and facilities and landform associated with historic and archeological resources. Efforts were intended to: (1) effectively predict the presence, quantity and quality of natural and cultural resources; (2) improve the knowledge of the basic processes of these resources as they relate to, and are impacted by, use of lands; and (3) advance the technology to mitigate, rehabilitate, and maintain these resources.

Alternate/Clean Energy

This area addressed the generation, transmission, use, and conservation of energy. DoD is the single largest user of energy in the world, with an annual energy consumption of more that 150 million barrels of oil equivalent at a yearly cost of more than $3.2 billion. The goals of this thrust area are to optimize the utilization of present energy sources; determine applicability of alternate energy sources for present energy usage systems and processes; and seek and/or develop replacements for present fuels with the specific goal being a renewable resource. Alternate/clean energy included research on environmentally sound alternative energy sources to reduce dependence on petroleum-based sources, overall energy consumption, energy costs and greenhouse effects.

Global Environmental Change

This Thrust Area focused on research which included acquisition/organization of data and research results that quantitatively described the total environment at global and regional scales. Integration of the new and existing programs in data collection and analysis methodologies, process study research and environmental modeling were keystones of this effort capitalizing on agency unique capabilities that fully leveraged the U.S. Global Change Research Program (USGCRP).

Global Environmental Change included improving access to existing DoD and DOE data bases and facilities; developing, demonstrating, and applying DoD, DOE, and EPA remote sensing capabilities and technologies to support environmental change

research and establish enhanced observation strategies and systems; and enhanced environmental process research and modeling. This area also focused on the employment of the DoD/DOE technical advantage and infrastructure toward understanding major environmental issues and recognizing the potential dual use application of this research, as directed by the SERDP authorizing language.

Pollution Prevention

Pollution Prevention means "source reduction," as defined under the Pollution Prevention Act of 1990 and other practices that reduce or eliminate the creation of pollutants through increased efficiency in the use of raw materials including energy, water and other resources, or materials substitution. The term includes: equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of materials and improvements in housekeeping, maintenance, training, or inventory control. Under the Pollution Prevention Act, end-of-pipe recycling, energy recovery, treatment, and disposal are not included within the definition of pollution prevention. Practices commonly described as "in-process recycling" qualify as pollution prevention.

Organization

Steps to reduce/eliminate duplication of effort began by ensuring that existing environmental programs were fully leveraged. Furthermore, to facilitate this leveraging, significant emphasis was placed on developing a management structure that was adequately familiar with the spectrum of technology efforts within the laboratories of the participating organizations.

The Council and their Executive Working Group directed the establishment of six Technology Thrust Area Working Groups (TTAWGs) to assist in building technically sound programs in each of the six thrust areas that are responsive to defense needs and fully complementary with other related programs. The membership of the TTAWGs reflected an appropriate and balanced distribution between SERDP participating organizations. Likewise, a similar balance was ensured between those that develop technology and those that implement this newly developed technology. Many of the DoD participants also served as participants in the Tri-Service Environmental Quality Strategic Research and Development Plan (EQ Strat Plan) Pillar development. The Executive Director of SERDP served in a dual role as Chairman of the Joint Engineers Management Panel and Reliance Environmental Quality Technology Panel. Thus, SERDP has taken advantage of an existing technology management structure to further identify and define R&D opportunities for investment in response to known requirements for R&D as developed by the Tri-Service's Reliance mechanism, and then provide sufficient resources to reach "critical mass" in order to address specific, difficult environmental challenges.

Initiatives

In FY 1993 the Department continued to build a closer coupling of DoD, DOE, and EPA research efforts. The intent was to focus on DoD/DOE needs by means of the SERDP management structure specified in the implementing legislation. Key SERDP initiatives for FY 1993 that build upon the joint approach include:

- National DoD Installation Restoration Technology Demonstration Sites;
- Joint DoD/DOE Program for Clean, Agile Manufacturing Technology for Propellants, Explosives and Pyrotechnics; and
- Pilot projects associated with the activities of the Gore-Gates Environmental Task Force.

National DoD Installation Restoration Technology Demonstration Sites

The recent emphasis placed on expediting remediation efforts of DoD/DOE facilities has likewise encouraged the development of novel remediation technologies. Unfortunately, their accomplishments have not been efficiently, nor effectively, transitioned to other technologists and the users within other Federal agencies and the private sector. Inconsistencies in the conduct of site characterization, data collection and assessment, and incomplete dissemination of the attributes and value of the demonstration have all contributed to this inefficient process.

One of the major initiatives commencing in FY 1993 is the establishment of six national DoD environmental technology demonstration sites. These sites will provide the ability to conduct side-by-side demonstrations of technologies developed either in the Federal or private sector. The National DoD Environmental Technology Demonstration Program (NETDP) offers an alternative to help reduce the duplication of effort and inefficiencies associated with the current system and promote rapid transfer of technology to field applications.

The NETDP uses the Reliance agreements as its foundation. It focuses on the demonstration of remediation technologies that respond to the primary needs of the Services. As the principal manufacturer of field weapons, the Army has been given the lead in the area of energetics materials remediation technology, and the Navy and Air Force have been given primary responsibility for technology development in the area of petroleum, oils, lubricants (POL) and solvents. Each development task is conducted within this Reliance framework which is subordinate to the Environmental Quality Technology Panel under the Joint Engineers coordinating committee.

While Reliance has provided a coordinating mechanism for the conduct of remediation technology development, it has not yet provided the support necessary to

bring together technologies for side-by-side comparison, standardization of data collection and analysis, and publication of user guides and engineering design specifications for scale-up. NETDP will accomplish this objective.

Joint DoD/DOE Program for Clean, Agile Manufacturing Technology for Propellants, Explosives and Pyrotechnics

The DoD is required to reduce the hazardous wastes associated with production of weapons systems using propellants, explosives, and pyrotechnics (PEP) by at least 50 percent by 1997. The DOE and the National Aeronautics and Space Administration (NASA) also have PEP waste reduction requirements. Approximately 500 million pounds of PEP are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/illuminators. PEP chemicals and products are produced in government operated, government-owned/contractor-operated (GOCO), and defense contractor facilities. Future waste reduction can be achieved by reducing wastes throughout the PEP product life cycle. The product life cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim, recover, and recycle excess material.

The goal of this initiative is to develop integrated product/process development (IPPD) technologies and tools to achieve a design for reconfiguring existing PEP production facilities into agile factories which will reduce total life cycle wastes by over 90 percent from the 1992 PEP waste baseline.

The technical approach is for governmental and industrial PEP R&D labs, pilot plants, and production facilities to be organized into a program network. Present products, processes, PEP chemicals, and technologies will be surveyed. Models and simulations will predict life cycle performance. Pollution prevention technologies and new factory concepts will be experimentally tested in existing facilities. The factory design will then be developed, including detailed descriptions of products, chemical engineering unit operations, utility requirements, regulatory and qualification approaches, safety, and pollution prevention devices to be used in its operation.

Gore-Gates Environmental Task Force (ETF)

The ETF was formed in response to a Congressional request to create a team of scientists with appropriate security clearances to work with the government and determine the applicability of classified systems and data to environmental science.

The scientists comprising the ETF have and are continuing to review:

- The environmental community's information needs;

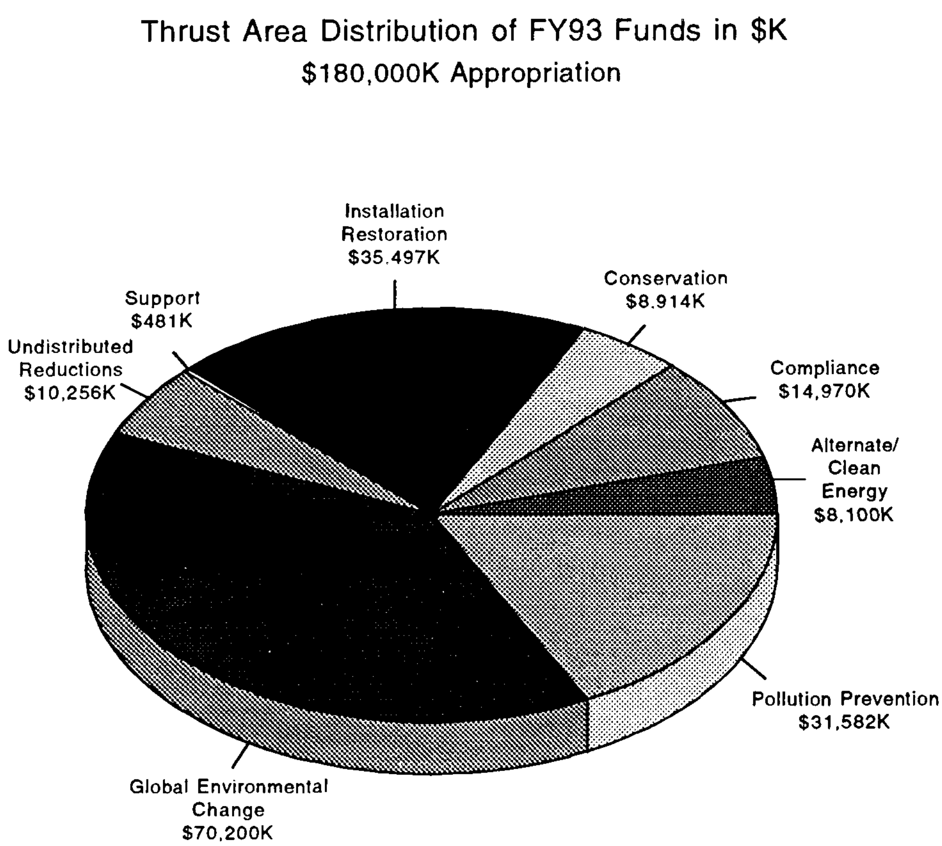
- Past, present, and near-term classified systems and data/archives; and
- Current government efforts that apply classified data to environmental issues.

The ETF scientists have recommended release of specific classified information of value to the environmental community, as well as follow-on research opportunities. An environmental security policy group has been activated with Service and Defense Agency participation. The Department has worked with the Intelligence community to develop procedures for competing environmental requirements on a routine basis for tasking of intelligence systems. These cooperative efforts have also resulted in the creation of a separate, highly successful Central Intelligence Agency (CIA) program designed to further leverage classified data opportunities with environmental considerations.

FY 1993 Project Summary

In FY 1993, there were 143 projects funded from a total of approximately 900 proposals. The distribution of funds across the thrust areas is shown in **Figure 1**.

Figure 1. SERDP FY93 Program Allocations



A summary of the FY 1993 Program funding distribution by Technology Thrust Area is shown in **Table I.** **Tables II through VII** show titles, executing organizations and actual FY 1993 funding received by the projects as approved by Congress and described in the *Strategic Investment Plan Fiscal Year 1993,* which was distributed in September 1993. Amounts made available to each Federal laboratory for the FY 1993 appropriations are shown in **Table VIII.**

TABLE I **FY 1993 FUNDING SUMMARY**	**Congressional Interest $(K)**	**Project Amount $(K)**	**FY93 Total Amount $(K)**
Installation Restoration	3,500	31,997	35,497
Compliance	2,333	12,637	14,970
Conservation	750	8,164	8,914
Alternate/Clean Energy	---	8,100	8,100
Global Environmental Change	5,000	65,200	70,200
Pollution Prevention	---	31,582	31,582
Undistributed Reductions			10,256
FY 1993 Scientific Advisory Board and Council Support			481
FY 1993 APPROPRIATION TOTAL			**180,000**

TABLE II **FY 1993 INSTALLATION RESTORATION PROJECTS**	**Actual Funding FY93 $(K)**
Characterization, Monitoring and Related Data Bases	
National DoD Environmental Technology Demonstration Program (A/AF/N/EPA)	5,970
Feasibility Study of an Environmental Technical Support Center (AF)	320
Landfill Characterization System Technologies Demo at Kirtland AFB RB11 Mixed Waste Site (DOE)	620
Consortium for Site Characterization Technology (EPA/DOE)	500
ECOTOX Data Base (EPA)	1,300
Advanced Fiber Optic-Based Spectroscopic Chemical Sensors for Cone Penetrometer (N/A)	425

TABLE II FY 1993 INSTALLATION RESTORATION PROJECTS	Actual Funding FY93 $(K)
Fate and Transport Methods and Models Development	
Simulation of the Impacts of Subsurface Heterogeneities on Remediation Effectiveness (A/EPA/AF/DOE)	4,310
Toxicology and Human Health Risks (AF/N/A/EPA)	1,500
Development of Military IRIS System for the Hazard Identification and Risk Assessment/Characterization of Defense Related Pollutants (EPA/AF/N)	1,000
Fuels in Soils and Groundwater	
Biodegradation Technology for Hazardous Waste Treatment (AF)	400
Enhanced Anaerobic Degradation of Jet Fuels in Groundwater (AF)	300
In Situ Aerobic Biodegradation of Hydrocarbon Fuels (AF)	400
Encapsulated or Immobilized Enzymes, Bacteria and Nutrients for Remediation of Fuel Spills (N)	350
Fuel Hydrocarbon Remediation (N)	895
In Situ Treatment of JP-5 Unsaturated Soils (N)	950
Solvents and Organics in Soils and Groundwater	
Air Sparging and In-Situ Bioremediation Integrated Project Demonstration at Picatinny Arsenal, NJ (A/USGS)	557
Enhancing Bioremediation Processes in Cold Regions (A)	500
Evaluation of the Semipermeable Membrane Device (SPMD) as a Passive In-Situ Concentrator of Military Organic Chemicals in Water (A)	50
Organophilic Clay Biosorption Treatment of Low Level Plasticizers and Solvents Contaminated Groundwater (A/AF)	500
In-Situ Abiotic Degradation of Solvent Contaminated Groundwater (AF)	700
Groundwater Cleanup of Organic Contaminants (TCE/PCE) Using Methanotrophic Bioreactors (DOE)	1,650
Demonstration of Enhanced Source Removal for Aquifer Restoration (EPA/AF)	2,200
Field Research at Wurtsmith AFB (EPA)	3,300
Treatment of Process Off-Gases Contaminated with TCE Using In-Situ Soil Based Aerobic Bioreactors (EPA/AF/A)	310
PCB Decontamination Using Base Catalyzed Decomposition Process (N)	400

TABLE II FY 1993 INSTALLATION RESTORATION PROJECTS	Actual Funding FY93 $(K)
Heavy Metals in Soils, Sludges, Sediments and Water	
Physical Separation Processes for Metal Contaminated Soils (A/N/DOE/DOI)	600
In-Situ Immobilization of Heavy Metals in Apatitic Minerals Formation (DOE)	350
Energetics in Soils and Groundwater	
Applied Demonstration Program in Environmental Compliance and Bioremediation Technology (A) *	3,500
Peroxone Treatment of Explosives Contaminated Groundwater (A)	570
Structures Decontamination	
Field Demonstration: Use of Hot Gas Technology to Decontaminate Excavated Underground Piping (A)	670
Application of the Base Catalyzed Dechlorination Process to Dechlorination of PCB Found on Navy Ships (EPA)	400
Installation Restoration Total	**35,497**

* Congressional Interest Program

TABLE III FY 1993 COMPLIANCE PROJECTS	Actual Funding FY93 $(K)
Maintenance Process Emissions	
Atmospheric Chemistry of Model AF Pollutant Compounds (AF)	255
Steady-state and Nonsteady-state Source NOx Emission Control (AF)	1,000
Combination Sorption/Catalyst Medium for Destruction of Halogenated VOCs - Dover Air Force Base (EPA)	500
Manufacturing and Disposal Emissions	
Energy Conservation and Air Toxic Compliance Plan for DoD Industrial Facilities (A)	550
Fundamental Studies of Thermal, Plasma, and Photochemical Processing for Waste Disposal Applications (A)	350
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	352
Fundamental Studies of Hazardous Metal-Ion Separations Chemistry (DOE)	450

TABLE III **FY 1993 COMPLIANCE PROJECTS**	**Actual Funding FY93 $(K)**
Kinetic Mechanisms for Supercritical Water Oxidation (DOE)	490
Dispersion in the Convective Boundary Layer (EPA)	200
Supercritical Water Oxidation of Hazardous Waste (N)	900
Open-Burning/Open Detonation of Explosives	
Advanced Testing of Emissions Produced During Open-Air Destruction of Energetic Materials (A/EPA/DOE)	568
Catalytic Extraction Processing of Energetic Wastes and Munitions (A)	600
Hydrothermal Reduction of Eroded and Intact Energetic Wastes (AF)	390
Solar Detoxification of Explosives in Water (DOE)	890
Operations and Training Emissions	
e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-products (DNA) *	833
ADVACATE Boiler Emission Control System (EPA)	1,250
Ship Emissions	
Shipboard Non-Oily Wastewater Treatment System (N)	1,325
Noise Impact Assessment	
Small Arms Range Noise Mitigation Technology Demonstration (A)	100
Turbulent Boundary Layer Effects on Sound Propagation (A)	175
Single Event Noise Exposure/Development and Human Response Prediction Model (AF/A/NASA)	350
Shore Management of Ship Wastes	
Contaminant Dispersal Model for San Diego Bay (N/A/USGS)	690
General Hazardous Waste Management	
Glassy Materials Modeling for Hazardous Waste Immobilization (A)	150
Portland-Cement Concrete Liners and Tanks for Isolating Hazardous Wastes (A)	90
Capacitive Deionization as a Means of Eliminating Secondary Wastes (DOE)	795
Waste Tank Remediation: Analysis and Waste Form Development (DOE)	217

TABLE III FY 1993 COMPLIANCE PROJECTS	Actual Funding FY93 $(K)
Technical and Economic Assessment of Storage of Industrial Waste on Abyssal Plains (N) *	1,500
Compliance Total	**14,970**

* Congressional Interest Program

TABLE IV FY 1993 CONSERVATION PROJECTS	Actual Funding FY93 $(K)
Natural and Cultural Resource Management	
Development of Overall Management Strategies for the Reduction of Noxious Plant Infestations with an Emphasis on Biological Control (A)	250
ITAM/Wetlands Integration (A)	450
Phased Array Ultrasonic Detection of Artifacts (A)	160
Land Scheduling and Management	
Digital Terrain Modeling and Distributed Soil Erosion Simulation/Measurement for Minimizing Environmental Impacts of Military Training (A/DOE)	800
Information Support for Environmental Management (A) *	750
Stabilization of High Use Training Areas in Cold Regions (A)	300
The Effects of Aircraft Overflights on Birds of Prey (AF)	80
Ecosystems Management	
Development of Regional Guidelines for Evaluating and Managing T&E Species Habitats on DoD Lands (A)	300
Identification, Assessment, and Mitigation of Impacts of Military-Related Chemicals and Pollutants on Threatened and Endangered Species (A/Forest Service/Fish & Wildlife Service)	525
LCTA/BCD Biological Diversity Sensitivity Analysis (A)	350
Methods for Propagation, Translocation, and Reestablishment of Threatened and Endangered Species (A)	350
The Role of Microphytic Soil Crusts in Desert Ecosystem Stability and Biodiversity (A/Forest Service/Park Service)	250

TABLE IV FY 1993 CONSERVATION PROJECTS	Actual Funding FY93 $(K)
Application of Biomarkers for Monitoring and Assessment of Sensitive Fauna in Ecosystems Impacted by Munitions Waste and Defense Related Material Application Sites (EPA/A/DOE/Fish & Wildlife Service)	900
Assessment and Management of Risks to Biodiversity and Habitat (EPA/USDA Forest Service)	1,000
Expanded Application of DNA Fingerprint Techniques Developed as Genetic Diversity Measures of Aquatic Populations (EPA/DOE)	200
Fishing Enforcement/Stock Assessment and Marine Mammal Monitoring (N)	2,000
Marine Mammal Health (N)	249
Conservation Total	**8,914**

TABLE V FY 1993 ALTERNATE/CLEAN ENERGY PROJECTS	Actual Funding FY93 $(K)
Applications of Alternate/Clean Energy Sources to DoD Facilities	
Fuel Cells for Military Applications (A)	350
Low Energy Model Installation Program (A)	1,400
Advanced Cycle Mobile Heat Pump (AF/DOE)	500
Geothermal Heat Pumps/Enhanced Building Envelopes (DOE/DoD)	600
Utilization of Biomass Technologies on Military Installations (EPA)	750
Photovoltaics for Military Applications (N/DOE/EPA)	4,000
Technology Demonstrations of Alternate/Clean Energy Sources	
Pilot Plant Demonstration of Methanol Using the HYDROCARB Process with Biomass Feedstock (EPA)	500
Alternate/Clean Energy Total	**8,100**

TABLE VI FY 1993 GLOBAL ENVIRONMENTAL CHANGE PROJECTS	Actual Funding FY93 $(K)
Remote Sensing	
Acoustic Monitoring of Global Environmental Change (ARPA)	24,000
Definition and Demonstration of Remote Sensing Capability to Contribute to Environmental Understanding and Support for Environmental Issues (DSPO/N/AF)	4,900
Environmental Task Force Research (DSPO)	2,000
Responsive Airborne Sensor Testbed for Environmental Research (Raster-J) (N/DSPO)	1,000
Joint DoD/DOE Atmospheric Remote Sensing and Assessment Program for Global Climate Change (N/DOE)	33,300
Data Manipulation Tools	
Strategic Environmental Distributed Active Archive Resources (N) *	5,000
Global Environmental Change Total	**70,200**

* Congressional Interest Program

TABLE VII FY 1993 POLLUTION PREVENTION PROJECTS	Actual Funding FY93 $(K)
Metal Working Processes	
Alternative Paint Stripper for Powder and Electrodeposition Coatings (A)	190
Alternative Process to Acid Cleaning/Degreasing of Depleted Uranium (A/DOE/AF)	125
Cadmium Plating Alternatives (A)	270
Environmentally Acceptable Heat Treating (A)	265
Investigation of Aqueous Cleaning Systems (A)	120
Nonchromatic/Noncarcinogenic Etching for Bonded Structures (A)	350
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A/N)	485
Waterjet Paint Stripping (A)	450
Electro Magnetic Powder Spray (AF)	300
Laser Cleaning and Coatings Removal (AF)	350

TABLE VII FY 1993 POLLUTION PREVENTION PROJECTS	Actual Funding FY93 $(K)
Non-Chemical Surface Preparation (AF/DOE)	300
Noncyanide Strippers to Replace Cyanide Strippers (AF)	1,100
Solid State Metal Cleaning (AF)	350
Electroplating Waste Reduction (N)	460
Recovery/Recycling/Purification of Plating/Cleaning Baths (N/AF/EPA)	600
Coatings and Applications	
Flame Spray of Thermal Plastic Coatings (A)	100
Investigate Water-Based Coating Systems for Military Clothing and Equipment (A)	130
Nonchromate Conversion Coatings for Aluminum Alloys (A)	245
Nonvolatile Organic Compound Chemical Agent Resistant Coating (A)	150
Accelerated Testing Techniques for Environmentally Acceptable Materials and Processes (AF)	100
Large Area Powder Coating (AF)	100
Aircraft Maintenance Chromium Replacement (N)	170
Innovative Very Low VOC Antifouling Paints and Processes (N)	570
Non-Hazardous, Low VOC Corrosion Protection Paints and Coatings (N)	3,500
Organic Protective Coatings and Application Technology (N)	490
Ordnance Processing	
Application of Supercritical Fluid Extraction and Supercritical Chromatography to Analysis of Energetic Materials (A)	200
Depleted Uranium Waste Minimization and Material Reutilization (A/AF)	350
Development of Non-Polluting Primary Explosives (A)	267
Continuous Oxide Reduction System (DOE)	371
Electron Beam Melting and In-Process Scrap Recycling of Uranium (DOE)	1,300
Plutonium and Uranium Metal Forming Technologies (DOE)	5,000
Joint DoD/DOE Program for Agile, Clean Manufacturing Technology for Propellants, Explosives, and Pyrotechnics (N/A/AF/DOE)	2,000
Ozone Depleting Substances Replacement	
Alternatives to Halon 1301 for Ground Vehicle Compartments (A)	1,524

TABLE VII **FY 1993 POLLUTION PREVENTION PROJECTS**	**Actual Funding FY93 $(K)**
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A)	300
Research in CFC Substitutes (A)	100
Encapsulated Micron Aerosol Agent Technology (AF)	650
High Efficiency Magnetic Bearing Lubrication-free Centrifugal Compressor for Use with Environmentally Safe Alternate Refrigerants (AF)	250
Evaluate Replacements for ODSs Used in Military Related Refrigeration Systems (EPA)	300
VOC and Hazardous Air Pollutant Emissions Reduction for Painting, Cleaning and Vapor Degreasing Facilities (EPA)	2,750
Ozone Depletion Potential (ODP) Calculations for Halon Replacement Compounds (NIST)	200
Hazardous Waste Reduction, In-Process Recycling or Elimination	
Alternate Solvents for Propellant Manufacture (A)	210
Elimination of Lead and Antimony Compounds in Solid Film Lubricants (A)	100
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)	400
An Environmental Knowledge Based Advisor for Facilities Life Cycle Decisions (EPA)	500
Evaluating Clean Technology Implementation (EPA)	500
Heavy Metal Discharge from Ship Ballast (N)	225
Propellant Recycling (N)	100
Solventless Pyrotechnic Manufacturing (N)	355
Packaging	
Verification of Shelf-life for Hazardous Materials (N)	200
Hazardous Materials Substitutes	
Advance Nickel-Metal Hydride Battery (AF)	300
Minimization of Solvents used in Analyzing Mixed or Hazardous Wastes (DOE)	360
Solvent Substitution and Low VOC Cleaners (N)	170
Non-Emulsifying Degreasers for Shipboard Use (N)	190

TABLE VII **FY 1993 POLLUTION PREVENTION PROJECTS**	**Actual Funding FY93 $(K)**
Data Bases	
Expanding the Pollution Prevention Information Exchange System (PIES) to Serve as a Communication and PP Network of Technical Information for Other Federal Agencies (EPA/DOE)	900
Reduce Greenhouse Gas Emissions	
Contribution of Mixing to Formation of NOx in Gas Turbine Compressors (AF)	240
Pollution Prevention Total	**31,582**

TABLE VIII **FY 1993 LABORATORY FUNDING**	**Actual Funding FY93 $(K)**
ARMY	
Construction Engineering Research Laboratory	8,850
Rock Island Arsenal	120
Armament Research, Development, and Engineering Center	2,367
Army Research Laboratory-Aberdeen Proving Ground	1,200
Army Research Laboratory-Warren	450
Army Research Laboratory-Watertown	1,000
Cold Regions Research & Engineering Laboratory	800
Missile Command, Redstone Arsenal	100
Tank Automotive Command-Research, Development, & Engineering Center	1,524
Topographic Engineering Center	850
Waterways Experiment Station	7,070
Dugway Proving Ground	568
Army Environmental Center	4,540
Biomedical R&D Laboratory	50
Natick Research Development & Engineering Center	230
ARMY TOTAL	**29,719**

TABLE VIII **FY 1993 LABORATORY FUNDING**	**Actual Funding FY93 $(K)**
AIR FORCE	
Human Systems Center	320
Armstrong Laboratory	7,575
Wright Laboratory	3,440
AIR FORCE TOTAL	**11,335**
NAVY	
Naval Command Control and Ocean Surveillance Center	1,934
Naval Air Warfare Center-China Lake	490
Naval Air Warfare Center-Lakehurst	170
Naval Surface Warfare Center-Carderock	1,325
Naval Surface Warfare Center-Indian Head	455
Naval Surface Warfare Center-Warminster	630
Naval Research Laboratory-Washington, D.C.	34,875
Naval Research Laboratory-Stennis Space Center	1,500
Naval Facilities Engineering Service Center	4,435
NAVY TOTAL	**45,814**
DEPARTMENT OF DEFENSE TOTAL	**86,868**
DOE	
New Brunswick Lab	360
Savannah River Technology Center	1,650
Los Alamos National Laboratory	5,450
Lawrence Livermore National Laboratory	2,466
Sandia National Laboratory-CA	1,110
Sandia National Laboratory-NM	4,600
Pacific Northwest Laboratory	567
Argonne National Laboratory	352

TABLE VIII **FY 1993 LABORATORY FUNDING**	**Actual Funding FY93 $(K)**
National Renewable Energy Laboratory	890
DOE TOTAL	**17,445**
EPA	
R.S. Kerr Laboratory	310
Environmental Research Laboratory-Duluth	1,300
Environmental Research Laboratory-Corvallis	1,000
Environmental Research Laboratory-Ada	2,200
Environmental Research Laboratory-Gulf Breeze	3,300
Environmental Monitoring Systems Laboratory-Cincinnati	1,100
Environmental Monitoring Systems Laboratory-Las Vegas	500
Atmospheric Research and Exposure Assessment Laboratory	200
Risk Reduction Engineering Laboratory	1,600
Air and Energy Engineering Research Laboratory	5,550
EPA TOTAL	**17,060**
OTHER FEDERAL RECIPIENTS	
Defense Advanced Research Projects Agency	24,000
Defense Nuclear Agency	833
Defense Support Projects Office	6,900
EPA Environmental Criteria & Assessment Office	1,000
EPA Office of Environmental Engineering & Technology Demonstration	900
National Institute of Standard and Technology	200
Naval Sea Systems Command	3,500
Office of Naval Research	7,000
Penn State University	1,000
Space and Naval Warfare Systems Command	2,000
U.S. Geological Survey	557
OTHER FEDERAL RECIPIENTS FUNDING TOTAL	**47,890**

TOTALS			
LABORATORIES			121,373
	DoD	86,868	
	DOE	17,445	
	EPA	17,060	
OTHER FEDERAL RECIPIENTS			47,890
UNDISTRIBUTED REDUCTIONS			10,256
FY 1993 SCIENTIFIC ADVISORY BOARD AND COUNCIL SUPPORT			481
TOTAL FY 1993 SERDP FUNDING			180,000

FY 1994 PROGRAM

Overview

FY 1994 focused on commencing a multi-year programming process; one that was developed and executed in a multi-agency management forum. This process began with the creation of a SERDP Strategic Guidance, a document that defined the six technology thrust areas, explained the concerns and goals of each area, and stated several broad research and development objectives. SERDP management developed a document which served as a means for the environmental community to focus on clear objectives and stated needs as provided by our field users. It also ensured that similar efforts were identified and leveraged, where appropriate.

In FY 1994, the six technology thrust areas remained. However, "Installation Restoration" was renamed "Cleanup" and "Alternate/Clean Energy" was changed to "Energy Conservation/Renewable Resources" to better match defense requirements. While the basic definitions of the thrust areas remained consistent with those in FY 1993, R&D objectives were developed, providing guidance to the R&D performer community and assisting in their proposal writing task. Where appropriate, direction was provided to the R&D community to ensure proper coordination with other Programs. For example, the proposal submitters for Global Environmental Change were directed to fully integrate their effort in the U.S. Global Change Research Program.

The SERDP Program proposal review process has been modified to further enhance coordination and avoid duplication. The Executive Director implemented several controls that ensured proper and adequate screening of proposals was being conducted at several levels, starting with the participating organizations. Proposals were reviewed extensively by both users and research and development staff within each

organization to determine relevance to defense needs and technical merit. Those proposals that survived this organizational review were submitted for competition with those submitted by the all participating organizations. Again the TTAWG forum was used to accomplish this process. The experts in each of the six TTAWGs reviewed proposals from all organizations with the specific charter of selecting proposals that best met the R&D objectives as stated in the Strategic Guidance. Concurrently, secondary objectives were to eliminate duplication and seek opportunities to combine proposals to form stronger alliances in quest to achieve the proposals' technical objectives. This review resulted in a prioritized list of projects that were submitted to the Executive Director via the SAB, which reviewed all projects that requested $900 thousand or more. In FY 1994, the SAB received a broad overview of the DoD environmental program to better calibrate their point of reference and assist in formulating their recommendations to the SERDP Council.

To complement the enhanced proposal review process, SERDP management increased their emphasis on project monitoring and execution by instituting an automated project tracking system using a relational data base. This data base has assisted in development of this report. Proposals are stored in a text base with full text retrieval capabilities designed to assist in the annual review of projects, the FY 1995/1996 program development process, and in forming an archive of SERDP projects. The SERDP Information Management Plan, has incorporated procedures and methods for transferring SERDP information electronically via Internet, thereby continuing attempts to share information and technologies developed by SERDP with other Federal and commercial entities.

Interagency Coordinating Bodies and Activities

In FY 1994 the Department is continuing to build a closer coupling of DoD, DOE and EPA research efforts. This approach to "program build" has resulted in an increase in cooperative/joint projects and a prevailing desire to further integrate projects with similar technical goals. Without exception, the TTAWG members recommended that a consistent membership on the Technology Thrust Area Working Group is essential to effect this program integration; a recommendation that has been implemented. Through the TTAWG coordinating mechanism, the efforts of the participating organizations will be leveraged, where possible, and duplication of effort eliminated.

Many of the TTAWG or Executive Working Group members are associated with one or more coordinating bodies that also focus on environmental concerns. They each bring this knowledge to the table during proposal reviews, annual in-progress reviews and program development meetings. For example, two DoD representatives on the President's Office of Science and Technology Policy's *National Science and Technology Committee* are also key members of the SERDP Executive Working Group. DoD and DOE both represent their positions on the Joint *Develop On-site Innovative Technologies*

(DOIT) Committee, a multi-agency, public/private coordinating body that promotes expediting waste site cleanup and the advancement of better remediation technologies. Four of the six DoD TTAWG Co-chairs are also the Chairs for the Services' Environmental Quality Pillars and were instrumental in the development and preparation of the FY 1995 EQ Strat Plan. Their first-hand knowledge in both Programs is essential for determining the complexion and content of the SERDP Program.

Changes in Military Specifications

To date, the Council has not recommended any changes in military specifications. However, there is a FY 1993 project that seeks to replace lead and antimony compounds in solid film lubricants (MIL-L-46147) with an environmentally compliant formulation. If this project is successful, this military standard would be revised accordingly. Other similar materials-substitution efforts may also result in military specification changes, or conversely, results from some of the projects may lead to changes in EPA's environmental regulations, which may mitigate the need for certain stringent military specifications.

Contracts, Agreements, of Other Documents for Cooperative Research and Development Activities

In the FY 1994 program there are six Cooperative Research and Development Agreements (CRADAs) identified; more are in the discussion phase. FY 1995 CRADAs have not yet been determined. Selected projects involving CRADAs are reviewed below.

<u>Elimination of Lead and Antimony Compounds in Solid Film Lubricants</u>

The goal of this Army project is to evaluate candidate formulations that could replace environmentally objectionable lead and antimony compounds for use in solid film lubricants and is funded in the Pollution Prevention thrust area.

There are two CRADAs in process for official signatures, with Sandstron Corporation and Tiodize Corporation. Another CRADA possibility is being reviewed by the legal section of EM Corporation; and a fourth CRADA is being pursued.

<u>Utilization of Biomass Technologies on Military Installations</u>

The goal of this project is to demonstrate an innovative energy conversion technology fueled with biomass at a DoD installation. It is a small-scale innovative energy conversion technology conducted by the EPA in the Energy Conservation/ Renewable Resources thrust area.

This technology could be easily deployed in both industrial and rural areas. The results would include reduced air emissions, minimized waste disposal, and cost savings in tipping fees as well as purchase of fossil fuels and electricity. It is also an exportable technology as it has applicability to Third World countries. Once technologies are selected (Fall of 1994), it is anticipated that a CRADA will be developed.

Combination Sorption/Catalyst Medium for Destruction of Halogenated Volatile Organic Compounds (VOCs)

The goal of this program is to continue development of an innovative adsorbing catalyst as an alternative for eliminating certain air emissions which occur during waste water cleaning operations. This is a cooperative effort between EPA and the Air Force in the Compliance thrust area.

A CRADA has been developed between EPA and Dr. Howard Greene of the University of Akron. It resulted from FY 1991 SERDP research into catalyst systems and has been in place since October 1992. Additional CRADAs are possible as this project investigates new sorption/catalyst systems, but all patents that result from this work belong to Dr. Greene.

Enhancing Bioremediation Processes in Cold Regions

The goal of this project is to improve remediation ability in areas subject to low temperatures. This project is a cooperative effort between the Army, EPA, and the State of Alaska in the Cleanup thrust area.

A CRADA is anticipated but is not in place as of yet. There have been discussions with private industry in areas where there are contaminated sites already in the process of cleanup.

Transferring Technology and Information

Transferring technology to the field is of paramount importance to the Department. SERDP is producing today the very technology that will offer improved remediation effectiveness at reduced costs to the government. It will also provide methods and processes that will virtually eliminate hazardous waste streams from many defense production operations.

Accordingly, significant emphasis is placed on transition/transfer during proposal evaluation and project monitoring. Each funded SERDP project was required to submit a Project Execution Plan that specified a technology transition/transfer plan in FY 1994 stating the specific products to be transferred, to whom and when. Each SERDP investigator was also requested to report on technology transition/transfer activities

during the planned SERDP Program Reviews and in required quarterly Progress Reports. Project proposals contained in the *Five-Year (1994-1998) Strategic Investment Plan* (Appendix A), describe various technology transfer items in the sections entitled, "Expected Payoff" and "Transition Plan."

During FY 1994, a SERDP brochure was developed to provide general information on the SERDP, defining and describing purposes and goals, and listing points of contact. This document has raised the awareness of the SERDP Program within the public domain. The near-term effects of this brochure are already being realized through increased interaction between private enterprises and the Federal laboratories.

Plans are in their final stages for publishing a SERDP newsletter that will disseminate both programmatic information as well as technical information to government and private recipients. As mentioned previously, efforts are underway to make SERDP information available via Internet. Our vision is to develop an interactive network used by all interested parties. Other opportunities for technology and information transfer to other government agencies and to nongovernmental organizations will be in the form of technical reports, journal articles, and conference proceedings. An annual SERDP conference is being planned which will be the principal forum for information transfer. Projects and their products that were developed by both Federal and private concerns will be exhibited, and a series of workshops will assist in conveying the prioritized environmental needs, the projects that are currently underway, and areas that may require special assistance from industry.

FY 1994 Proposal Summary

Of the 1300 proposals that were submitted by Federal laboratories and other agencies requesting SERDP funding in FY 1994, 752 were forwarded by the participating Federal managing organizations to the Executive Director and TTAWGs for further review and consideration. A breakdown of proposed funding across the thrust areas is shown in **Figure 2**. The Plasma-Arc Disposal Facility for medical waste, a Congressional interest item, was not an appropriate effort for funding within the SERDP and consequently, $1,875 million was withheld. This project would fund the design and construction of a waste disposal facility using proven technology; the investment strategy for the SERDP focuses on research, technology development, and technology demonstration. The FY 1994 projects approved by the Council are described in the *SERDP Five-Year (1994-1998) Strategic Investment Plan* (Appendix A), including project duration and estimated cost.

A summary of the FY 1994 funding by thrust area is shown in **Table IX**. **Tables X through XV** show project titles, executing organizations and FY 1994 funding requested and approved by the Council. Amounts made available to each Federal laboratory for the FY 1994 appropriations are shown in **Table XVI**.

Figure 2. SERDP FY94 Program Allocations

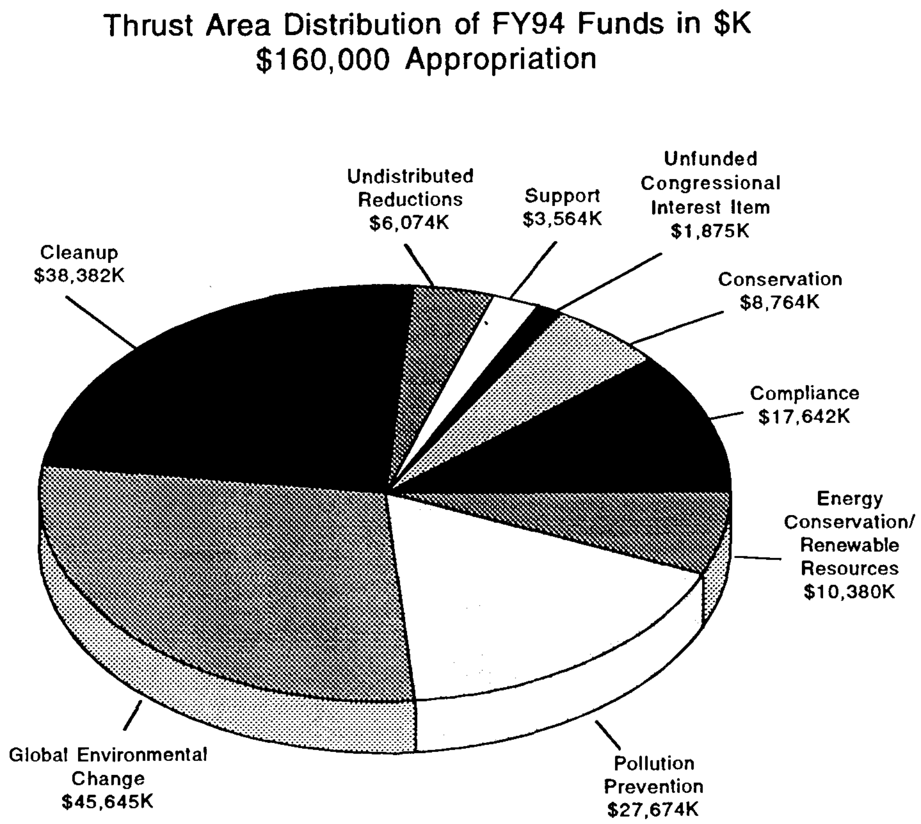


TABLE IX **FY 1994 FUNDING SUMMARY**	**Congressional Interest $(K)**	**Project Amount $(K)**	**FY94 Total Amount ($K)**
Cleanup	4,000	34,382	38,382
Compliance	3,950	13,692	17,642
Conservation	---	8,764	8,764
Energy Conservation/Renewable Resources	---	10,380	10,380
Global Environmental Change	1,250	44,395	45,645
Pollution Prevention	---	27,674	27,674
FY 1994 Scientific Advisory Board and Council Support			3,564
Undistributed Reductions			6,074
Unfunded Congressional Interest Item			1,875
FY 1994 APPROPRIATION TOTAL			**160,000**

TABLE X FY 1994 CLEANUP PROJECTS	Actual Funding FY94 $(K)
Characterization, Monitoring, Modeling, Measurement, Methods - Field	
Accelerated Tri-Services SCAPS Sensor Development (A)	3,375
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)	290
Field Portable FTS Fiber Optic VOC Sensor (AF)	55
Real Time Neural Network Raman Signal Enhancement (DOE)	180
Integrated Characterization Program Combining DOE (PNL) UFA and DoD (NRAD) Sensor Technologies (DOE)	300
Silica Fiberoptic Probe for Site Characterization (DOE)	435
Subsurface Gas Flowmeter (DOE)	125
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA)	280
Subsurface Bioremediation Process Monitoring Indicators (EPA)	550
In Situ "Inside-Out" NMR Sensor for Contaminant ID (N)	450
Mobile Underwater Debris Survey System (N)	1,400
Rapid Detection of Explosives and Other Pollutants (N)	100
Hazard Risk Assessment, Modeling, Methodologies - Fate/Transport Models	
Toxicology and Human Health Risks (AF)	1,400
Hazard Risk Assessment, Modeling, Methodologies - Methodology and Protocol	
Hazard Assessment Techniques and Biomonitoring Technology (A)	1,745
Treatment Technologies - Groundwater/Surface Water	
Biosorption Treatment of Plasticizers and Solvents (A)	750
Enhancing Bioremediation Processes in Cold Regions (A)	700
Peroxene Treatment of Contaminated Groundwaters (A)	950
Aerobic Bioremediation of a Contaminated Aquifer (AF)	630
Air Waste Stream Treatment Technologies (AF)	700
Bioremediation of Hydrazine/Energetic Materials (AF)	420
Catalytic In Situ Treatment of Chlorinated Solvents (AF)	720

TABLE X FY 1994 CLEANUP PROJECTS	Actual Funding FY94 $(K)
Joint US/Germany In-Situ Bioremediation Demonstration (AF)	450
Aquifer Restoration by Enhanced Source Removal (EPA)	2,200
Removal and Encapsulation of Heavy Metals from Ground Water (EPA)	350
Encapsulated Bacteria for In Situ PAH Bioremediation (N)	350
In Situ Bioremediation of Fuel and Efficacy Monitoring (N)	2,450
Treatment Technologies - Soils/Sludges	
Air Sparging and In-Situ Bioremediation Research (A)	557
Explosives Conjugation Products in Remediation Matrices (A)	500
Integrated Biotreatment Research Program: From Flask to Field (A)	2,450
Surfactant-Enhanced Biodegradation of Contaminants (A)	700
Cleanup of TRU Contaminated Soils with CO_2 Soluble Ligands (DOE)	50
Fuel Hydrocarbon Remediation (N)	550
Other	
National Environmental Technology Test Sites Program (A)	8,220
Northeast Institute for Environmental Remediation (A) *	4,000
Cleanup Total	**38,382**

* Congressional Interest

TABLE XI FY 1994 COMPLIANCE PROJECTS	Actual Funding FY94 $(K)
Boiler/Engine Emissions	
Metal Perovskite Catalysts for NOx Reduction (AF)	175
Steady-State/Nonsteady-State NOx Emission Control (AF)	850
e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-Products (DNA)	2,600
Compact, Closed-Loop Controlled Waste Incineration (N)	1,000
Reduction of NOx Emissions from Marine Power Plants (N)	750

TABLE XI FY 1994 COMPLIANCE PROJECTS	Actual Funding FY94 $(K)
General Hazardous Waste Management	
Lead-Based Paint Hazard Mitigation (A)	700
Emission Reduction Planning Model (AF)	200
Laser Ablation/Ionization Characterization of Solids (DOE)	380
Vapor Permeation VOC Recovery from Refueling and Storage (EPA)	250
Solid Waste Encapsulation (DOE) *	100
Monitoring	
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)	500
Leak Location in Underground Pipelines (EPA)	1,000
Air Quality Monitor (AF) *	350
Noise Impacts	
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)	550
Open Burning/Open Detonation	
Characterization Open Burning/Open Detonation Emissions (A)	1,128
Measuring and Modeling for OB/OD Permitting (EPA)	350
Physical Treatment Processes	
Hydrothermal Reduction of Energetic Wastes (AF)	375
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	380
Kinetics of Supercritical Water Oxidation (DOE)	740
Waste Forms Based on Separations Media (DOE)	200
Supercritical Water Oxidation of Organic Wastes (N)	364
Shipboard Emissions	
Shipboard Non-Oily Wastewater Treatment System (N)	400
Waste Minimization/Recycling	
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A)	800

TABLE XI FY 1994 COMPLIANCE PROJECTS	Actual Funding FY94 $(K)
Other	
National Environmental Education and Training Center (NEETC) (A) *	3,500
Compliance Total	**17,642**

* Congressional Interest

TABLE XII FY 1994 CONSERVATION PROJECTS	Actual Funding FY94 $(K)
Community Ecosytem - Management	
Landscape Watershed/Ecosystem Management (A)	1,140
Strategic Natural Resource Management Methodology (DOE)	433
Multiple - Risk/Impact Assessment	
Assessment and Management of Risks to Biodiversity and Habitat (EPA)	1,325
Species/Genetic - Management	
Threatened, Endangered and Sensitive Resources (A)	805
Species/Genetic - Resource Characterization	
Fishing Enforcement/Whale Monitoring Using IUSS (N)	3,000
Species/Genetic - Risk/Impact Assessment	
The Effects of Aircraft Overflights on Birds of Prey (AF)	311
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)	800
Genetic Diversity Monitoring in Plants and Wildlife (EPA)	200
Marine Mammal Health Monitoring (N)	250
Watershed/Landscape - Management	
Strategy for Resource Management on DoD/DOE Lands Combined with Decision Support for Disturbed Ecosystem Renewal (DOE)	500
Conservation Total	**8,764**

TABLE XIII FY 1994 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS	Actual Funding FY94 $(K)
Energy Conservation	
Low Energy Model Installation Program (A)	1,650
Natural Gas Based Air Conditioning Demonstration (A)	230
Advanced Cogeneration and Absorption Chilling (DOE)	300
Optimize Energy Efficiency of AC Induction Motors (EPA)	250
Renewable Energy	
Fuel Cells for Military Applications (A)	350
Advanced Cycle Mobile Heat Pump (AF)	850
Thermal Acoustic Piezoelectric Power Generator (DNA)	100
Geothermal Space Conditioning for Large DoD Buildings (DOE)	800
Clean Liquid Fuel from Biomass and Carbonaceous Wastes (EPA)	500
Utilization of Biomass Technologies on Military Installations (EPA)	750
Low Emissions Shipboard Fuel Cell Power Plants (N)	600
Photovoltaics for Military Applications (N)	4,000
Energy Conservation/Renewable Resources Total	**10,380**

TABLE XIV FY 1994 GLOBAL ENVIRONMENTAL CHANGE PROJECTS	Actual Funding FY94 $(K)
Air/Ocean Interface Research	
Global Ocean Monitoring and Prediction (GOMAP) (N)	900
Atmospheric Research	
Comparison of CIRRIS 1A and UARS/ATMOS Databases (AF)	395
Environmental Requirements for Cloud Analysis (DSPO)	800
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE) *	24,700

TABLE XIV FY 1994 GLOBAL ENVIRONMENTAL CHANGE PROJECTS	Actual Funding FY94 $(K)
Ocean Research	
Acoustic Monitoring of Global Ocean Climate (includes GAMOT) (ARPA) *	17,000
Terrestrial Research	
Global Inventory of Biomass Burning (EPA)	600
Other	
Strategic Environmental Distributed Active Archive Resources (SEDAAR) (N) *	1,250
Global Environmental Change Total	**45,645**

* Congressional Interest

TABLE XV FY 1994 POLLUTION PREVENTION PROJECTS	Actual Funding FY94 $(K)
Coatings	
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)	550
Electro Magnetic Powder Spray (AF)	630
Large Area Powder Coating (AF)	315
Alternative Coatings for Cadmium Plating of Small Parts (N)	800
Fluorinated Ship-Hull Coatings for Non-Polluting Control (N)	895
Organic Protective Coatings and Application Technology (N)	400
Data Base	
Integrated Expert Solvent Substitution Data Base (EPA)	3,000
Diagnostic	
Rapid Testing for Acceptable Materials and Processes (AF)	263
Life Cycle Engineering and Design Program (EPA)	750
Model for Facilities Life Cycle Decisions (EPA)	400

TABLE XV FY 1994 POLLUTION PREVENTION PROJECTS	Actual Funding FY94 $(K)
Hazardous Materials Substitutes	
Advanced Zinc Phosphate Metal Pre-Treatment (A)	175
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)	300
High-Performance, Lead-Free Electrical Sealants (DOE)	110
Reduce VOCs and HAPs from Painting and Cleaning Operations (EPA)	600
Aircraft Maintenance Chromium Replacement (N)	180
Dry Nitrogen for Ship Boiler Layup (N)	185
Solvent Substitution and Low VOC Cleaners (N)	150
Hazardous Materials Processing	
Non-Chemical Surface Preparation (AF)	998
Solid State Metal Cleaning (AF)	1,050
Hazardous Waste Reduction	
Large Aircraft Robotic Paint Stripping (LARPS) (AF)	1,940
Laser Cleaning and Coatings Removal (AF)	2,100
Aircraft Depainting Technology (N)	445
Recycle Boiler Nitrite Solution (N)	475
Mixed Waste	
Acid Recycle (DOE)	258
Capacitive Deionization for Elimination of Wastes (DOE)	700
Metal Working Process	
Alternate Electroplating Technology (N)	360
Recycling/Purification of Plating/Cleaning Baths (N)	800
Ordnance Processing	
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)	450
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)	200
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)	350

TABLE XV FY 1994 POLLUTION PREVENTION PROJECTS	Actual Funding FY94 $(K)
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N)	3,700
Solventless Pyrotechnic Manufacturing (N)	500
Ozone Depleting Substances	
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A)	400
Chemistry of Halon Substitutes (A)	155
Continuous Aqueous Cleaning to Eliminate ODC (A)	110
Non Ozone Depleting Sealants for Ammunition Applications (A)	250
Replacements of Hydrochlorflurocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)	250
Advanced Streamlining Agent (AF)	850
Encapsulated Micron Aerosol Fire Suppression Technology (AF)	630
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)	1,000
Pollution Prevention Total	**27,674**

TABLE XVI FY 1994 LABORATORY FUNDING	Actual Funding FY94 $(K)
ARMY	
Construction Engineering Research Laboratory	4,285
Rock Island Arsenal	110
Armament Research, Development, and Engineering Center	807
Army Research Laboratory-Aberdeen Proving Ground	1,845
Army Research Laboratory-Watertown	850
Cold Regions Research & Engineering Laboratory	700
Tank Automotive Command-Research, Development, & Engineering Center	175
Topographic Engineering Center	250

TABLE XVI FY 1994 LABORATORY FUNDING	Actual Funding FY94 $(K)
Waterways Experiment Station	17,365
Dugway Proving Ground	1,128
Army Environmental Center	9,020
Biomedical R&D Laboratory	1,745
ARMY TOTAL	**38,280**
AIR FORCE	
Armstrong Laboratory	6,031
Wright Laboratory	9,681
Phillips Laboratory	1,545
AIR FORCE TOTAL	**17,257**
NAVY	
Naval Command Control & Ocean Surveillance Center	1,595
Naval Air Warfare Center	5,000
Naval Surface Warfare Center-Carderock	1,750
Naval Surface Warfare Center-Dahlgren Division	1,400
Naval Surface Warfare Center-Indian Head	500
Naval Surface Warfare Center-Warminster	1,535
Naval Research Laboratory	3,800
Naval Facilities Engineering Service Center	2,374
NAVY TOTAL	**17,954**
DEPARTMENT OF DEFENSE TOTAL	**73,491**
DOE	
Brookhaven National Laboratory	400
Los Alamos National Laboratory	258
Lawrence Livermore National Laboratory	880
Oak Ridge National Laboratory	935
Sandia National Laboratory-CA	25,565

TABLE XVI **FY 1994 LABORATORY FUNDING**	**Actual Funding FY94 $(K)**
Sandia National Laboratory-NM	910
Pacific Northwest Laboratory	880
Argonne National Laboratory	813
Idaho National Engineering Laboratory	50
DOE TOTAL	**30,691**
EPA	
R.S. Kerr Laboratory	2,750
Environmental Research Laboratory	1,325
Environmental Monitoring Systems Laboratory-Cincinnati	1,000
Environmental Monitoring Systems Laboratory-Las Vegas	600
Atmospheric Research and Exposure Assessment Laboratory	350
Risk Reduction Engineering Laboratory	2,630
Air and Energy Engineering Research Laboratory	3,500
EPA TOTAL	**12,155**
OTHER FEDERAL RECIPIENTS	
Advanced Research Projects Agency	17,000
Defense Nuclear Agency	2,700
EPA Office of Environmental Engineering & Technology Demonstration	3,000
McClellan AFB	700
Naval Sea Systems Command	800
Office of Naval Research	4,950
Space and Naval Warfare Systems Command	3,000
OTHER FEDERAL RECIPIENTS FUNDING TOTAL	**32,150**

TOTALS			
LABORATORIES			116,337
	DoD	73,491	
	DOE	30,691	
	EPA	12,155	
OTHER FEDERAL RECIPIENTS			32,150
FY 1994 SCIENTIFIC ADVISORY BOARD AND COUNCIL SUPPORT			3,564
UNDISTRIBUTED REDUCTIONS			6,074
UNDISTRIBUTED CONGRESSIONAL INTEREST ITEM			1,875
TOTAL FY 1994 SERDP FUNDING			160,000

Additional Recommendations or Proposals to Congress

There are no additional recommendations or proposals to Congress.

FY 1995 PROGRAM

The Department has requested $111.9 million in the FY 1995 President's budget. Actual amounts requested for FY 1995 by Federal laboratories will be determined after a review of ongoing efforts is conducted by the SERDP Program Office during the Summer of 1994 and approval of the FY95 Program by the SERDP Council.

TABLE A-I **FY 1994 CLEANUP PROJECTS**	**FUNDING $(K) FY94**	**ID Number**	**Page Number**
Characterization, Monitoring, Modeling, Measurement, Methods - Field			
Accelerated Tri-Services SCAPS Sensor Development (A)	3,375	729	A-4
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)	290	713	A-9
Field Portable FTS Fiber Optic VOC Sensor (AF)	55	103	A-12
Real Time Neural Network Raman Signal Enhancement (DOE)	180	621	A-15
Integrated Characterization Program Combining DOE (PNL) UFA and DoD (NRAD) Sensor Technologies (DOE)	300	592	A-19
Silica Fiberoptic Probe for Site Characterization (DOE)	435	741	A-23
Subsurface Gas Flowmeter (DOE)	125	404	A-27
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA)	280	371	A-31
Subsurface Bioremediation Process Monitoring Indicators (EPA)	550	383	A-34
In Situ "Inside-Out" NMR Sensor for Contaminant ID (N)	450	38	A-39
Mobile Underwater Debris Survey System (MUDSS) (N)	1,400	52	A-44
Rapid Detection of Explosives and Other Pollutants (N)	100	28	A-49
Hazard Risk Assessment, Modeling, Methodologies - Fate/Transport Models			
Toxicology and Human Health Risks (AF)	1,400	115	A-53
Hazard Risk Assessment, Modeling, Methodologies - Methodology and Protocol			
Hazard Assessment Techniques and Biomonitoring Technology (A)	1,745	717	A-58

TABLE A-I FY 1994 CLEANUP PROJECTS	FUNDING $(K) FY94	ID Number	Page Number
Treatment Technologies - Groundwater/Surface Water			
Biosorption Treatment of Plasticizers and Solvents (A)	750	711	A-64
Enhancing Bioremediation Processes in Cold Regions (A)	700	712	A-69
Peroxone Treatment of Contaminated Groundwaters (A)	950	726	A-73
Aerobic Bioremediation of a Contaminated Aquifer (AF)	630	95	A-80
Air Waste Stream Treatment Technologies (AF)	700	131	A-82
Bioremediation of Hydrazine/Energetic Materials (AF)	420	118	A-85
Catalytic In Situ Treatment of Chlorinated Solvents (AF)	720	107	A-88
Joint US/Germany In-Situ Bioremediation Demonstration (AF)	450	99	A-92
In-Situ Chemical Treatments for Enhanced Subsurface Cleanup (DOE)	0	430	A-95
The Engineering Design of In Situ Bioremediation (DOE)	0	514	A-100
Aquifer Restoration by Enhanced Source Removal (EPA)	2,200	368	A-105
Removal and Encapsulation of Heavy Metals from Ground Water (EPA)	350	387	A-109
Encapsulated Bacteria for In Situ PAH Bioremediation (N)	350	23	A-113
In Situ Bioremediation of Fuel and Efficacy Monitoring (N)	2,450	30	A-117
Treatment Technologies - Soils/Sludges			
Air Sparging and In-Situ Bioremediation Research (A)	557	744	A-122
Explosives Conjugation Products in Remediation Matrices (A)	500	715	A-126
Integrated Biotreatment Research Program: From Flask to Field (A)	2,450	720	A-129

TABLE A-I **FY 1994 CLEANUP PROJECTS**	**FUNDING $(K) FY94**	**ID Number**	**Page Number**
Treatment Technologies - Soils/Sludges			
Surfactant-Enhanced Biodegradation of Contaminants (A)	700	731	A-136
Cleanup of TRU Contaminated Soils with CO_2 Soluble Ligands (DOE)	50	447	A-141
Fuel Hydrocarbon Remediation (N)	550	20	A-144
Other			
National Environmental Technology Test Sites Program (A/AF/N/EPA)	8,220	723	A-149
Northeast Institute for Environmental Remediation (A) *	4,000	818	A-155
Cleanup Total	**38,382**		

* Congressional Interest

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Accelerated Tri-Services SCAPS Sensor Development

3. **Agency:** Army

4. **Laboratory:** U.S.A.E. Waterways Experiment Station (WES)

5. **Proposal ID:** #729

6. Problem Statement:

Currently, site characterization represents a significant portion of remediation efforts, accounting for approximately one-third of the total costs. Environmental site characterization has been traditionally based on drilling, sampling, and laboratory analysis. Complete delineation of subsurface contaminants usually requires trial-and-error placement of a significant number of monitoring wells and extensive sample collection efforts. Laboratory analysis of samples taken in the field is time consuming, costly, and often imprecise due to site history, contaminant profiles, and biogeochemical interactions. This traditional approach to site characterization hampers remediation efforts because of its uncertainty, time requirements, and cost.

The Site Characterization and Analysis Penetrometer System (SCAPS) was developed to address many of these deficiencies. SCAPS combines traditional cone penetrometer technology with contaminant and geophysical sensors to rapidly provide a profile of contaminants and geophysical properties in a cost effective manner. The SCAPS has progressed under sponsorship of the Tri-Services and DOE, and is an ideal platform for advanced sensor systems.

There exists a critical need to develop advanced sensor technologies to characterize sites containing metals, POL's, solvents, explosives, and radioactive contaminants. In order to maximize their payoff in future remediation efforts, it is critical that environmental sensors be developed and transitioned as rapidly as possible. This proposal addresses the need to accelerate the research, development, and demonstration of sensor, sampling, and associated data processing technologies for SCAPS.

7. Project Description:

The goal of the accelerated sensor program is to develop technologies for detecting and delineating contaminants and for characterizing geophysical properties in situ. This Tri-Service program is leveraged with supporting research sponsored by DOE and EPA. It includes a comprehensive and jointly executed set of tasks to significantly accelerate the development of sensors for the SCAPS system. The proposed work partially fulfills SCAPS Thrust milestones as identified in the FY93 Tri-Service Environmental R&D Strategic Plan.

Under the proposed scope of work, the Tri-Services will accelerate the development of new sensor systems that will expand the capability of the SCAPS for in situ detection of chemical contamination. Additionally, the proposed work includes development of improved sampling, analysis, and processing technologies to support the enhanced sensor technologies. Some of the

proposed work will continue efforts supported under FY93 SERDP funding. The following are the primary thrusts for this project:

(1) Laser-Induced Breakdown Spectroscopy (LIBS). A fiber optic based LIBS system using pulsed laser energy to generate plasma from solid and liquid samples is being developed jointly by the DoD. Emission spectra from the plasma provides simultaneous multi-element analysis of metals including Zn, Cr, Pb, Cu, Ni and Cd. However, several technical challenges remain to be overcome before LIBS technology is viable for SCAPS implementation. The research effort proposed includes; (a) evaluate potential approaches for in situ generation of the plasma in the soil with the penetrometer probe, (b) characterize and optimize the fiber optic delivery system for the laser pulse, and (c) develop software techniques for detecting atomic line spectra of heavy metals (d) develop neural network pattern recognition schemes for processing spectral emission data.

(2) Fiber Optic Raman Sensor (FORS). A prototype Raman sensor system is currently being evaluated for measurement of selected volatile aromatic hydrocarbons and solvents in soils. Technical issues include sensitivity and interferences from fluorescence components in the sample. Sensitivity enhancements will be accomplished by improvements in sensor and probe design. Wavelength shifting of the Raman excitation source will be evaluated for minimizing interferences from background fluorescence. Multiple wavelength and tunable laser sources will be developed and tested as a means of minimizing fluorescence background signals and for performing resonance enhanced Raman spectroscopy.

(3) Improved Laser-Induced Fluorescence (LIF) Sensor. The Tri-Services are currently evaluating new laser sources and detectors for improving the existing LIF sensors for POL contaminant detection. In order to enhance both the sensitivity and range of POL contaminants detected, the following research efforts will be conducted: (a) evaluate multiple wavelength UV sources including Raman shifters and Optical Parametric Oscillators as alternatives to the current dye lasers, and (b) increase the amount of information collected by LIF SCAPS probes including the capability to acquire complete time resolved excitation-emission matrices. Additionally, the feasibility of laser based sensors for detection of explosives in soils by photofragmentation/LIF methods will be investigated.

(4) Electrochemical Sensors. Electrochemical sensors for detecting volatile organic compounds (VOC) and low concentrations of explosives contaminants are currently being developed. These sensors presently require probes that provide thermal energy necessary to vaporize or desorb volatile and semi-volatile contaminants in situ for detection. Development of these probes and interfacing with electrochemical sensors will require extensive laboratory testing to fully characterize operation and robustly compare electrochemical sensor results to conventional methods. The laboratory testing will encompass a number of soil matrices to identify and mitigate possible interference sources, and to quantify their detection limits. Subsequent development efforts may be required to improve sensor performance and overcome soil matrix effects.

(5) Spectral Gamma Probe. A SCAPS spectral gamma probe for detection of radioactive wastes is currently under development by DoD for DOE. Enhancements to the detector hardware, signal conditioning, and data processing will be made to increase sensitivity and selectivity, and to better characterize the collected emission spectra. Laboratory tests will be conducted to define and document system performance.

(6) Sampling Technology. Improved and innovative sampling technology to enhance the capability to collect soil, groundwater, and vapor samples using SCAPS will be developed. A critical issue common to all sampling technology is analyte behavior in the region of the sampler. An extensive laboratory testing program based on the multiport sampler technology previously developed will be used as a base to describe analyte behavior. Multi-port sampling technology will be developed to increase sampler range to an umbilical length of 45 meters. Analyte behavior will be related to contaminant pressure and concentration consistent with site characterization objectives, and sampler performance will be fully characterized for diverse geophysical environments. Coupling sampler technology to surface analytical instrumentation will be investigated including such methods as extraction into an inert carrier gas with an infrared heated flexible fused quartz transporter column.

(7) Data Processing Methodologies. Data acquisition, analysis, and visualization software for SCAPS will be developed to fully exploit the capabilities of the emerging sensor and sampler technologies. Developed software will include a data base management system, graphic display capability, geostatistical decision analysis, and an interface to groundwater and contaminant transport decision analysis models. The approach will be to develop a basic set of software tools which can be used to evaluate the contaminant distribution and site stratigraphy, locate subsequent sounding and sampling locations, provide a data base of all pertinent site data, and graphically display all site data in three dimensions.

(8) Technology Demonstration and Implementation. This accelerated program of sensors development will aggressively move to demonstrate the sensors on the SCAPS platform. Tri-service demonstrations, coordinated by the U.S. Army Environmental Center will be performed on VOC and improved laser-based fiber optic sensors in FY94/95. Field tests will be conducted on the fiber optic Raman sensor (FORS) in FY95.

8. Expected Payoff:

Proposed work will provide the DoD and DOE an expanded scope of sensor and sampling technologies coupled with data processing and analysis software tools for SCAPS. Immediate payoff will be technology for VOC, explosives, and heavy metal contaminant detection, and improved POL detection. Improved SCAPS sampling technology will provide alternative cost effective methods to obtain site characterization and verification data. Hybrid sampling technologies coupled to sensors and in situ methods for contaminant extraction will greatly expand the utility of SCAPS technology. The Tri-Service SCAPS will serve as a test platform for all technology development and will accelerate the evaluation of effectiveness and feasibility for subsequent demonstration activities. Rapid development of sensor technologies for SCAPS will significantly increase its return on investment (ROI).

9. Milestones:

(Assuming 10/93 start)

Complete initial development of electrochemical probes for VOC's and explosives	06/94
Complete development data processing methodology	06/94
Complete EPA demo of LIF POL sensor	08/94
Complete improved gamma sensor	09/94
Complete improved LIF POL sensor development	10/94
Complete initial field evaluation of electrochemical probes	10/94

Complete fabrication of prototype Raman (FORS) probe	10/94
Complete initial laboratory testing of VOC sampler	11/94
Complete design of LIBS probe	12/94
Complete LIBS software development	01/95
Complete improved LIF/POL sensor demonstrations	02/95
Complete initial testing of improved gamma sensor	02/95
Complete development of enhanced data acquisition, analysis and visualization software	05/95
Complete FORS software development	06/95
Complete design of advanced FORS probe	06/95
Complete fabrication of LIBS prototype probe	06/95
Complete testing and user review of enhanced software	09/95
Complete field demonstrations of FORS sensor	10/95
Complete laboratory testing of analyte behavior	10/95
Complete photofragmentation/LIF explosives sensor	10/95
Complete tests of VOC sampler interface to analytical instrumentation	11/95
Complete initial description of analyte behavior in soil	03/96
Evaluate quantitative aspects of SCAPSsampler technology	09/96
Complete field tests of LIBS metal sensor	09/96
Complete field demonstrations of photofragmentation/LIF sensor	09/96

10. Transition Plan:

Technology developed under this proposed effort will be transitioned to the Army's Environmental Center (AEC) which is the agency responsible for demonstrating and transitioning SCAPS technologies to the U.S. Army Corps of Engineers District Offices, the Naval Facilities Engineering Command, the Air Force System Program Office (HSC/YAQ), and DOE. This provides a conduit for all developed technology to DoD and DOE through a comprehensive plan that includes demonstration, documentation, training, and technical support. Transition of SCAPS technology to private industry will be pursued by licensing agreements for patented technology and though Cooperative Research and Development Agreements (CRADA).

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
AF	825	600	400	0	1825
ARMY	1700	1400	1250	0	4350
NAVY	850	850	700	0	2400
TOTAL SERDP	3375	2850	2350	0	8575

12. Performers:

SCAPS development is primarily a Tri-Service activity including the Army (U.S.A.E. Waterways Experiment Station, Army Environmental Center), AF (Armstrong Laboratory, AF Center for Environmental Excellence), and the Navy (NCCOSC). Additional performers include DOE, EPA, and private industry and Universities.

13. Principal Investigators:

ARMY:
Dr. Ernesto Cespedes
USAE Waterways Experiment Station
CEWES-EE-S
3909 Halls Ferry Road
Vicksburg, MS 39180-6199
(601) 634-2655 VOICE
(601) 634-2732 FAX

ARMY:
Mr. George Robitaille
Army Environmental Center
SFIM-AEC-TSC, Bldg E4435
Aberdeen Proving Ground, MD
21010-5401
(410) 671-1576 VOICE
(410) 671-1680 FAX

NAVY:
Dr. Stephen H. Lieberman
NCCOSC RDT&E Division 521
53475 Strothe Road
San Diego, CA 92152-6325
(619) 553-2778 VOICE
(619) 553-6305 FAX

AIR FORCE:
Mr. Bruce Nielsen (AL/EQW)
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
(904) 283-6011 VOICE
(904) 283-6090 FAX

14. Keywords:

SCAPS, Sensor, Environmental Sensors, Samplers, Site Characterization, Contaminant, Remediation.

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Cleanup

2. Title: The Sensitive Detection of Unexploded Ordinance and other Hazardous Materials

3. Agency: Army

4. Laboratory: Army Research Laboratory, Aberdeen Proving Ground, MD

5. Proposal ID: #713

6. Problem Statement:

The development of laser-based, analytical sensors for the rapid detection and monitoring of trace atmospheric vapors in real-time has been of great interest in recent years. Environmental issues pertaining to pollution prevention, compliance, and cleanup have been important driving force behind this development. Another related issue deals with the detection of trace atmospheric vapors of energetic materials such as explosives and propellants. This is not to surprising given the potential civilian and military applications for these developing technologies in aviation security, demilitarization, and cleanup activities. The overall objective of this proposal is to develop and deploy a reliable and cost-effective apparatus for the sensitive detection of energetic materials as well as toxic halogenated compounds and heavy metals as identified by the Major Range and Test Facility Bases (MRTFB) Environmental Coordinating Committee (MECC).

7. Project Description:

At the 1992 Army Science Conference, we presented a paper which received first prize and was awarded the Paul A. Siple Memorial Award. In this paper, we described a novel technique for sensing trace atmospheric vapors of energetic materials and chemical agent simulants. This technique (patent pending) is based on the use of one laser operating to both photofragment the target molecule and detect the characteristic fragments by resonance-enhanced multiphoton ionization (REMPI) and/or laser-induced fluorescence (LIF). The analytical utility was demonstrated on a number of compounds, including TNT and RDX, employing molecular beam mass spectrometry. A detection limit of 8 and 24 parts-per-billion (ppb) was obtained for RDX and TNT, respectively, using only 100 µJ/pulse of laser energy.

A literature review of the electronic transitions of NO reveals that they are also resonant with 193 nm or 222 nm radiation, the output from an excimer laser. The advantages of using this laser over that used previously is that it is more rugged, more compact, and readily fieldable. In addition, the out put is approximately a few thousand times more than the 226 nm radiation used for the detection of TNT and RDX. As a result, we expect to improve substantially on our limits of detection of these and other energetic materials. For this proposal we plan the following:

- Replace 226 nm laser system with a compact excimer laser.
- Replace our molecular beam time-of-flight apparatus (approximately 64 ft^3) with a hand held optogalvanic detector. In addition to reducing the size of the apparatus, a ten to one hundred fold increase in sensitivity is projected due to direct atmospheric sampling.

- Replace 226 nm laser system with a compact excimer laser.
- Replace our molecular beam time-of-flight apparatus (approximately 64 ft^3) with a hand held optogalvanic detector. In addition to reducing the size of the apparatus, a ten to one hundred fold increase in sensitivity is projected due to direct atmospheric sampling.
- Add a cryogenic stage for enhanced selectivity and modify sample delivery for enhanced sensitivity.
- Extend this technique for the detection of volatile organic compounds (VOC's).
- Fabricate and deploy prototype.
- Identify source of pollutants for cleanup/remediation actions.

Complementary conventional monitoring techniques such as x-ray fluorescence and atomic absorption will also be used if needed.

This project is presently being supported by an ARL Independent Laboratory Innovative Research Award and leveraged by SBIR funds.

8. Expected Payoff:

Potential Users: DoD, DOE, EPA, FAA, Custom and Postal Services, and other agencies involved with the ultrasensitive detection of energetic materials or pollutants.

Benefits:

- A rapid and ultrasensitive, real-time, laser-based detector which will have both military and civilian applications. Excellent potential for opening up new commercial and military markets.
- Reduction of costs of cleanup/remediation for sites containing energetic materials, heavy metals, and halogen-containing compounds.
- Increased safety to personnel working at site or involved with cleanup activities.

9. Milestones:

a. Replace apparatus components for enhanced performance and deployment. Laboratory testing and demonstration. Establish Cooperative Research and Development Agreements with other potential users, i.e. NAVY, DOE, EPA, FAA. (12 months)

b. Fabricate prototype. Initiate transition of technology to the Army Safety, Health, and Environmental Directorate, as well as other DoD and FAA users. (12 months)

c. Deploy prototype. Identify source of pollutants and assist in cleanup/remediation actions. (12 months)

10. Transition Plan:

Technology transfer would take place via the Army Safety, Health, and Environmental Directorate. Cooperative Research and Development Agreements with Navy, DOE, EPA, FAA, and various industries would be established. Financial support for transitions would result from ARL and DSHE, leveraged by Stablelase, Inc., Polymicro, Inc., and General Fiber Optics, Inc. via

SBIR Phase II Projects. Funds from other agencies requesting sensor technology are also projected.

11. Funding: ($K)

FY94	FY95	FY96	Total
290	320	345	955

Leveraged Funds Supplied by other Sources:
$145,000, FY94, ARL Independent Laboratory Innovative Research Award
$585,000, from currently funded SBIR Program Stablelase, Inc. Phase II SBIR: Small, Compact Field-Worthy Excimer and Solid State Laser Systems. Contract DAAA15-93-C-0074.

$590,000, from Polymicro, Inc. Phase II SBIR: High Performance Ultraviolet Infrared Optical Fibers, Contract DAAA15-93-C-0122.
$744,000, from currently funded SBIR Program, General Fiber Optics, Inc. Phase II SBIR: Optical Fiber Feedthrough/Connectors. Contract DAAA15-93-C-0068.

12. Performers:

Drs R.C. Sausa, B.E Forch, and H. Rogers, ARL Senior Staff; Drs. G. Lemire and J. Simeonsson, NRC/NAS Postdoctoral Research Associates; Dr. James Baily, Safety, Health, and Environment Directorate (DSHE), Aberdeen Proving Ground, MD; Professor Kenneth Ledingham, Department of Physics, University of Glasgow, Scotland, UK; Professor A. Amirav, Dept. of Chemistry, Tel Aviv University, Israel; Stablelase, Inc., SBIR Phase II: General Fiber Optics, Inc., Polymicro, Inc.

13. Principal Investigators:

Dr. Rosario C. Sausa
Co-Investigator: Dr. J. Simeonsson
US Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005
Phone: (410) 278-7070 Fax: (410) 278-9734

14. Keywords:

Laser photofragmentation/Ionization spectroscopy

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Field Portable FTS Fiber Optic VOC Sensor

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory

5. **Proposal ID:** #103

6. Problem Statement:

The goal of this project is to develop a prototype field portable Fourier Transform spectrometer that will detect and measure the presence of volatile organic compounds (VOCs) in soil at hazardous waste sites and long term compliance monitoring stations. Rapid on site screening of soils for VOCs can be accomplished by analyzing Raman or laser-induced fluorescent signatures. This project builds a new type of Fourier Transform Spectrometer (FTS) that marries a fiber-optic light delivery and collection system with a compact optical design that requires no mechanical scanning. The spectrometer is based on a miniature common-path interferometer and a unique solid-state light sensor that provides light detection and spectral processing on a single integrated circuit. The prototype's monolithic FTS chip will also be tested for dual-use applications in laser warning receivers, IFF, and laser communications configurations.

VOC sorption in soil depends on the availability of bonding sites, and the amount of mineral surfaces, organic matter, and moisture in the soil. This creates problems when trying to determine the actual VOC concentration in a particular sample. Current analysis protocols mitigate this problem by calling for bulk soil collection taken from the hazardous waste sites to be shipped to laboratories. At the laboratory, sub samples are drawn from the bulk sample and analyzed by purge-and-trap gas chromatography/mass spectrometry (EPA SW-846, method 8240). To overcome the soil property variances and rapidly characterize a hazardous waste site, the ideal instrumentation for in situ VOCs determination would allow multiple VOCs of interest to be identified and measured simultaneously in real time. Additionally, such an instrument should be hand-held and should not use water as an extractant or dispersion medium (to avoid displacing the VOCs). Direct spectral measurement of VOC analytes using remote spectroscopy techniques would avoid sample preparation involving water.

This program will be a new effort for WL/AAWP-3 building on current developments for FTS spectrometry and integrated imaging/signal processing devices currently under development by Remote Spectral Capture.

7. Project Description:

This project investigates feasibility of producing a ruggedized instrument package that includes a set of fiber optic sensors with coupling to a proprietary FTS configuration comprised of a miniature common path interferometer and proprietary imager/signal processing chip. The

objective is to develop an instrument that will have sufficient performance to support VOC detection in a field environment.

The technical approach to this effort will include the use of a proven method of obtaining the spectral signatures of target contaminants including a fiber optically coupled FTS. Spectrochemical analysis will be used to characterize the optical signatures of the contaminants and develop appropriate and effective detection algorithms. The Proof-of-Concept investigation will focus on trichloroethylene (TCE), Benzene (Ben), and Toluene (Tol) because they are frequently encountered due to use in industrial solvents and petroleum products and are on the EPA 17 Target Chemicals Lists.

This program's effort will be a synergistic combination of integrated research spectrochemical analysis, detection and identification algorithms, optical design, and novel detector design and fabrication.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust; 1C Characterization and Monitoring.

8. Expected Payoff:

This device will have dual-use application, with potential government and commercial users. Potential users would have a need to detect, categorize, and measure VOCs and HAZMATS. The impact of this device would be a device capable of mapping VOC concentration contours at hazardous waste sites or EPA soil pollution limit compliance monitoring at DoD and DoE facilities and throughout the industrial base. The FTS chip/interferometer design will be of important and immediate use for priority laser warning receiver research on single aperture laser warning receivers and combined missile warning/laser warning receivers.

9. Milestones:

1.	Breadboard FTS fabrication	10/93
2.	Complete review of detection methods	04/94
2.	Estimated Contract Commencement date	07/94
3.	Detection and recognition algorithms definition	09/94
4.	Laser subsystem/interferometer designs	02/95
5.	Interferometer fabrication and FTS chip design	06/95
6.	FTS chip/electronics fabrication	08/95
7.	Prototype hardware integration and validation	12/95
8.	Final report and prototype hardware delivered	03/96

10. Transition Plan:

WL/AAWP-3 LWR EO Laboratory will be the Government agency managing the program. The development contractor and CRADA partner will be Remote Spectral Capture. Validation testing in the interested instrument-manufacturing firms will lead to cooperative opportunities for technology transfer to the commercial market. Potential users will be involved in all aspects of the test execution and post test analysis.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	55	110	65	230

12. Performers:

This project will be a cooperative research and development (CRADA) effort between RSC and WL/AAWP-3. RSC will perform the FTS chip design and oversee foundry fabrications of the chip. RSC and WL/AAWP-3 will share interferometer design, prototyping, testing and calibration tasks as well as detection and algorithm development. Final integration, laboratory and field testing will be accomplished at the WL/AAWP-3 nationally recognized Electro-Optics, Laser Test Facilities.

13. Principal Investigator:

Matthew P. Dierking
WL/AAWP-3
Hangar 4B, 3050 C Street
Wright-Patterson AFB, Ohio 45433-7300
Commercial: 513-255-2471, DSN: 785-2471

14. Keywords:

Stationary interferometer, Fourier-transform spectrometer, Fiber Optic, Interferometry, Surface enhanced Raman scattering, Spectrochemical analysis

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Real Time Neural Network Raman Signal Enhancement

3. **Agency:** DOE

4. **Laboratory:** LLNL

5. **Proposal ID:** #621

6. **Problem Statement:**

There exists a great need for site investigation technologies that provide waste location and characterization in real time. Raman spectroscopy is a vibrational technique which can be used to identify molecular structure in solids, liquids, and on surfaces. It is relatively insensitive to water, making it an ideal technique for identifying molecular contaminants in aqueous solutions. While Raman is a powerful tool in chemical identification, some weak points exist. The first is inherent in the Raman experiment itself, where the efficiency of the Raman signal is only about 10^{-8} of that of the excitation light. This results in measurements where the signal to noise ratio can be quite low, often obscuring important spectral information. The second is in the processing of the vibrational data, which can involve large, time consuming multivariant analysis programs as the complexity of the mixture being monitored increases. Herein we propose the development of a real time multispectral analysis system based on hardware that is being developed by an industrial partner that can extract data from extremely high noise and identify individual components of complex mixtures.

7. **Project Description:**

A novel Raman spectrometer shall be developed that utilizes Neural Network (NN) signal processing to extract the chemical signatures of VOCs from spectra exhibiting extremely high noise levels. The Raman system shall be used to both identify and quantify DOE/DoD target contaminants in both solid samples and ground-water, with a secondary application being the location and identification of subsurface NAPLs. The system will utilize a Neural Network package that is being developed by Physical Optics Corporation (POC) for real-time signal extraction from high background noise in conjunction with a remote Raman spectrometer. The POC Neural Network is unique in that it is based on VLSI digital parallel processing HARDWARE rather than a software package. The advantage of the hardware approach is the greatly reduced processing time involved (30 milliseconds for complex spectral input). The NN shall be "trained" to recognize the spectral features of organic compounds such as aromatic and chlorinated hydrocarbons at concentration levels ranging from ppb in water to neat liquids, and inorganic complexes such as ferri- and ferrocyanide in aqueous and solid inorganic matrices. A field portable unit shall be delivered for deployment at new and existing DoD/DOE waste sites to identify and measure contaminants in situ. Preliminary OHER funded research has demonstrated the successful application of NN to Raman spectroscopic problems. The identification of individual components of complex chlorocarbon mixtures in the presence of signal to noise levels of less than 1:1 has been performed, as well as the observation of marked

enhancement of the lower limit of concentration levels of organic contaminants detectable by Raman spectroscopy in solution (10000 ppm carbon tetrachloride by conventional Raman vs 100 ppm (V/V) using a thermal electrically cooled OMA and NN data extraction). These analyses were demonstrated in real time, with five component mixtures with a signal to noise level of less than 1:1 being fully identified in under 1 second per spectrum. Continued refinement of the NN package will yield enhancement of the sensitivity levels by potentially three orders of magnitude.

The tasks within this project can be summarized as follows:

Training Data Acquisition: In FY93, Raman data for preliminary work with POC (OHER funding) was obtained with a laboratory Raman system consisting of a water cooled argon ion laser, table mounted optics, a SPEX 0.75 meter monochromator, and a Princeton Instruments TE cooled Optical Multichannel Analyzer (OMA). The current proposal requires a new library of Raman spectra of target organic compounds to train the POC Neural Network shall be obtained utilizing a field deployable Raman system. One such system has been developed at LLNL for the DOE/OTD UST-ID(TTP 2112-03). 'This system consists of an air cooled Ar ion laser for Raman excitation, a compact Chromex 0.25 meter imaging monochromator with optics mounted directly to the monochromator, and fiber optics which couple the monochromator and the laser source to various geometries of Raman probes. The detector is a Princeton Instruments liquid N_2 cooled CCD camera, which offers an improvement of S/N by a factor of 10-100 over the OMA. We shall also survey commercially available portable Raman systems to determine the best system to be utilized in this study. Once a system has been chosen, a library shall be constructed consisting of the Raman spectra organic and inorganic target compounds, particularly chlorocarbons including CCl_4, $CHCl_3$, CH_2Cl_2, TCE, PCE, and TCA, gasoline components (BETX), inorganics nitrates, nitrites, and cyanides. The matrix will include spectra of each compound at various aqueous and solid solution concentrations to train the Neural Network to recognize individual species quantitatively.

Optimization of Neural Network Designs and Algorithms: Building on algorithms and experience obtained in FY93, POC shall continue to improve the sensitivity of their Neural Network based Smart Optical Spectrum Analyzer (SOSA). Using the data from the field deployable fiber optic Raman system obtained as described above, POC shall investigate various algorithms, such as matched filtering, wavelet analysis and multichannel correlation, for optimizing S/N of the input/output signals. Neural Network models will be selected to train the system with large numbers of compounds to subsequently extract and emphasize special features of the Raman spectral signals. Different techniques will be compared and optimized combinations will be selected based on accuracy of spectral identification, rejection of noise, accuracy of compound quantification, and processing speed.

Real-Time Testing of Neural Network with Remote Raman System:
POC shall deliver the optimized Neural Network Spectrum Analyzer to LLNL for evaluation under laboratory conditions using the Fiber Optic Remote Raman Spectrometer. The ability of the Neural Network to accurately identify and quantify organics as neet liquids, mixtures, and aqueous solutions shall be analyzed. The Neural Network shall also be required to sense and characterize organics under various environmental conditions such as temperature, pH, turbidity, and different exposure times. Data obtained at this stage shall be used to further refine the Neural Network.

LLNL Field Demonstration: A field deployable version of the Neural Network shall be integrated with the field Raman system. The combined unit shall be tested at LLNL's site 300 for characterization of aqueous TCE levels and TCE NAPLs. Groundwater monitoring wells at LLNL main site will be used to demonstrate the utility of the system for TCE detection below 100 ppm.

DOE/DoD Site Demonstration: The Neural Network and Raman system shall be used at DOE/DoD sites for real-time identification and quantification of the components of the complex chlorocarbon contaminants in the groundwater. DNAPLs shall be mapped, if applicable. In addition, identification of inorganic components of UST core samples at the Westinghouse Hanford Site shall be performed in conjunction with the UST-ID Raman program Experience gathered at the test sites shall be used to define a practical instrument for real-time, ultrasensitive simultaneous detection, identification, and quantification of environmentally significant compounds at DOE/DoD hazardous waste and remediation sites.

8. Expected Payoff:

The success of this program shall result in a commercially available spectral analysis package to be manufactured and marketed by POC. While this proposal deals specifically with the application of the POC Neural Network to Raman Spectroscopy, the successful completion of this project will also serve as a proof of principal that the Neural Network can be universally applied to spectrographic techniques in general, eventually leading to the utilization of the spectrum analysis in Mass Spectrometry, Infra-red Spectroscopy, etc. The end deliverable to the DOE/DoD will be Raman instrumentation that can be used for qualitative and quantitative real time analysis of the components in environmental contamination sites.

9. Milestones:

1.	Survey of commercially available deployable Raman systems	3/94
2.	Purchase/construction of deployable Raman system	5/94
3.	Complete training data acquisition	7/94
4.	Optimization of Neural Network designs and algorithms	10/94
5.	Real time testing of Neural Network with Raman system	12/94
6.	LLNL field demonstration	3/95
7.	Integration with Hanford UST-ID Raman system	6/95
8.	Hanford field demonstration	8/95
9.	DOE/DoD site demonstrations for ground water contaminants	12/95
10.	Final system delivery	4/96

10. Transition Plan:

The original Neural Network technology was developed by POC under an SBIR to the army for target pattern recognition. The development continues as an in house program at POC, leading to eventual commercialization of the Neural Network for use in government, industrial, academic, and medical communities. The application of the Neural Network to environmental problems was a joint venture between LLNL and POC. The final transfer of technology from the laboratory to the field shall entail the purchase of the Neural Network system from POC as the commercial vendor.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	180	250	250	680
DOE	0	0	0	0
TOTAL	180	250	250	680

12. Performers:

The performers, including the Principal Investigator listed in item 13, are Dr. Kevin R. Kyle, Dr. Thomas M. Vess of DOE-LLNL and Dr. Tai-Wei Lu. Dr. Kyle is an environmental analytical chemist who specializes in the applications of spectroscopy to the identification and measurement of environmental contaminants. His main areas of research involves the use of fiber optics in remote chemical and Raman sensing. Dr. Vess is a staff scientist at LLNL who has been involved in the conception and design of both field deployable Raman spectrometer, one of which was delivered to Westinghouse Hanford as a milestone in FY93, and fiber optic Raman probes. Dr. Lu is a staff Research Scientist at Physical Optics Corporation, and is the key person involved in the development of the POC Neural Network technology.

13. Principal Investigator:

Dr. Kevin R. Kyle
LLNL
P.O. Box 808, L-524
Livermore, CA 94551
TEL: (510) 423-3693
FAX: (510) 422-8020
kyle2@llnl.gov Email

14. Keywords:

Raman Spectroscopy, Neural Network, Spectral Analysis, Real Time Detection, Signal Extraction, Signal Enhancement.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Integrated Characterization Program Combining DOE (PNL) UFA and DoD (NRAD) Sensor Technologies

3. **Agency:** Department of Energy

4. **Laboratory:** Pacific Northwest Laboratory (PNL)

5. **Proposal ID:** #592

6. **Problem Statement:**

Defining the nature and extent of subsurface chemical contamination is a costly and time-consuming process at sites requiring remediation. Detailed site investigations require installation of many monitoring wells and subsequent analysis of discrete soil and groundwater samples. Effective site characterization is often limited by the ability to select optimal locations for monitoring wells. Furthermore, the ability to resolve horizontal and vertical features in the distribution of chemical contaminants and to determine the transport rates of these contaminants in various stratigraphic layers is a function of limitations imposed by the spacing between wells and the vertical spacing between samples. At present, locations for monitoring wells are usually based on information gleaned from site historical data, ground water hydrology, and/or indirect chemical screening such as soil gas measurements. Because of the limitations of these methods, many wells are not properly positioned and, therefore, yield information of marginal utility. By utilizing a cone penetrometer (CPT) mounted sensor technology it is possible to obtain continuous coverage over the investigated depth intervals and more precisely delineate the boundaries of contaminant plumes, thus it is less likely that "clean" material will be unnecessarily removed or subjected to costly remediation procedures.

Although determining the current position of contaminant plumes is important, obtaining the information necessary for predicting future contaminant movement may be of even greater long term importance. Knowledge of the transport characteristics of soils (including hydraulic conductivity) under unsaturated and saturated conditions is required for modeling the transport of contaminants in subsurface materials surrounding hazardous and mixed waste sites. Once the nature and extent of the contamination are determined, it is also necessary to understand the transport properties of the soil to determine the potential risk to public health and environment that will ultimately control the degree and time frame of remediation. If stratigraphic horizons where future contaminant transport will likely occur can be identified, remediation efforts can be more efficiently directed. The hydraulic conductivity of soil depends strongly on the characteristics of the fluid and substrate, and on the volumetric water content of the soil. Traditionally, it has been difficult to obtain transport data on unsaturated and multicomponent systems because of the long experimental durations (weeks to years) necessary for achieving hydraulic steady state. By using the Unsaturated Flow Apparatus (UFA), it is possible to experimentally measure transport characteristics in a very short time frame (hours to days) under the wide range of conditions that exist in the field.

This proposal is for a new, applied research program that couples two relatively new characterization techniques to provide a more powerful characterization procedure. Both techniques stress innovative technologies that allow rapid completion of the installation characterization procedure so that planning future remediation programs may be done in a more cost effective manner. The first technology is the CPT mounted sensors that rapidly delineate contaminant plume boundaries in the subsurface. Developed through a Triservice DoD collaboration, the Site Characterization and Analysis Penetrometer System has been successfully employed for characterization at several DoD installations. The second technology is the UFA, a system that allows rapid determination of subsurface transport parameters in porous media. It was developed at DOE's Pacific Northwest Laboratories (PNL) for use at many DOE sites, including characterization studies at the Hanford Site.

7. Project Description:

This project is structured to develop and demonstrate the synergistic integration of two characterization techniques. The project scope is divided into two phases. This phased approach will allow continual refinement and streamlining of the interactions between the two government laboratories. The initial phase will include a pilot-scale demonstration of the current capabilities of both systems to aid in the planned development of sensor technology that will better evaluate the soil matrix. This development includes work at NRAD on new optical based imaging systems to evaluate grain size distribution that will improve the textural determinations (sand, silt, clay) currently made by CPT point and sleeve resistances. This matrix sensor will optically image the soil matrix at depth, providing a digitized image from which grain size distribution (and pore geometry) can be derived. Additional sensor development will focus on determinations of soil moisture content. The work at PNL will focus on determining the sensitivity of hydraulic conductivities to the variations in soil textural data properties that the CPT with new sensors can detect. This will determine how many representative soil types will be required for UFA measurement to sufficiently characterize the hydraulic properties at a selected field site. The digitized soil matrix images can then be used to develop image analysis programs as input to models for deriving hydraulic transport properties over the full range of soil types observed at a site. The second phase of the project will involve the field scale demonstration of the capabilities of the combined techniques. An installation will be selected based on the type of contaminant (compatibility with developed sensors) and soil textures (initially a limited range in soil texture variations) present at the site. The CPT will be deployed with a combination of sensors and will recover soil samples from representative stratigraphic horizons for UFA studies. Continuous matrix image analysis and moisture content data over the investigated depths will allow continuous determinations of fluid transport properties across the site. As the field demonstration progresses, evaluation of the data will indicate where additional CPT deployments are required to obtain detailed information from specific stratigraphic horizons.

During both phases of the program industrial partners will be working with the laboratories so technology transfer opportunities to promote commercialization will be possible.

8. Expected Payoff:

The potential benefit of this project is the development of a superior, rapid characterization program that will allow a more cost effective remediation plan to be developed. The CPT sensor technology is a more rapid, cost effective method to delineate contaminant boundaries than

traditional well drilling. The UFA technology is a more rapid, cost effective method to directly determine transport parameters (required for estimating or modeling contaminant movements) than other traditional techniques. Direct determinations are preferable to any estimation techniques because estimations are often overly conservative and lead to extremely expensive remediation programs. By developing the process in conjunction with an industrial partner, commercially available applications could be possible in the near term.

9. Milestones:

All dates based on January 1994 start:

1.	Complete pilot-scale sensor and UFA studies	6/94
2.	Demo CPT sensor and UFA method at field-scale	9/94
3.	Complete bench-scale work on CPT optical imaging system	6/95
4.	Field-scale demo of combined CPT and UFA method	6/96
5.	Assess and evaluate results of demo	9/96

10. Transition Plan:

PNL will be the lead laboratory for this project. During the initial phase, a contaminated site will be identified for demonstration and participation in the development of the coupling process between these techniques so that the site will be available for later phase field operations. Both laboratories are involved with industrial partners in attempts to transfer these technologies to the private sector.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	300	300	350	950

12. Performers:

The proposed project will be managed by PNL. Battelle operates PNL for the Department of Energy.

An industrial partner that provides field CPT support is currently working with NRAD. It is anticipated that they will participate in the development and field demonstration of the process to facilitate technology transfer. An industrial partner has already agreed to work with PNL on commercialization of the UFA through the CRADA process. Demonstration of the coupled technologies will assist in commercialization of the UFA and CPT sensor technologies by demonstrating the additional utility of the combined techniques. This should help to provide the means for near-term industrial applications.

13. Principal Investigators:

JV Wright, PhD
Mail Stop B1-34
Battelle-PNL
Richland, WA 99352
TEL: (509) 375-3268
FAX: (509) 375-4838

JM Leather, PhD
Mail Stop B1-34
Battelle-PNL
Richland, WA 99252
TEL: (509) 375-3268

SH Lieberman, PhD
NRAD
Code 522
San Diego, CA 92152
TEL: (619) 553-2778
FAX: (619) 553-6305

14. Keywords:

Characterization, Contaminant, Transport, Sensors, UFA, CPT

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Silica Fiberoptic Probe for Site Characterization

3. **Agency:** Department of Energy

4. **Laboratory:** Oak Ridge National Laboratory

5. **Proposal ID:** #741

6. **Problem Statements:**

This project is to develop improved techniques for locating, characterizing, and monitoring hazardous wastes in a timely, cost-effective manner as pointed out in the SERDP cleanup thrust. The innovative part of this project relies on the use of a unique all-silica fiberoptic spectral probe that we have initially developed for monitoring the soluble magnesium ion concentration in molten salts of interest to the electrochemical magnesium process industry. The probe is essentially a silica rod which maintains the characteristics of the individual optical fibers, from 2 to 7, of which it is composed. No glues, epoxy materials, or adhesives are used in the probe; such materials can result in stability problems, chemical or radiation, that are not shown by a pure silica material. This device has proven useful for spectral measurements in molten salts; it has the potential of many applications in the area of environmental analysis. In this project the probe will be coupled with commercially available components, in cooperation with EIC Laboratories, Inc., to make a portable instrument that will be field tested at various sites and process monitoring locations of interest to DOE, including the waste tanks of the Hanford site and in wells and locations on the Oak Ridge reservation. This probe should be very sensitive to heavy metals, various classes of organic compounds, biological contaminants and poisons. EIC Laboratories is already funded through the Morgantown Energy Technology Center of DOE under a project "Field Raman Spectrograph for Environmental Analysis." This new project involves applied research and an expanded technology demonstration.

7. **Project Description:**

We have developed an all-silica fiberoptic probe for use in monitoring the soluble magnesium concentration, as $MgCl_4^{-2}$, in molten $NaCl$-KCl-$CaCl_2$-$MgCl_2$ (35-35-15-15 mole%) at 700°C by Raman spectroscopy. We have also developed a normalization technique, based on comparing all spectra to the magnitude of the Rayleigh line scattering, to quantify this measurement. Because of the nature of the fabrication, this probe can be considered essentially a quartz rod that maintains the characteristics of the individual optical fibers of which it is composed. In preliminary studies the probe has been useful for obtaining Raman spectra over a temperature range of from 77 to 1200K, fluorescence spectra to 77K, reflectance spectra (of solids) from 77 to 1300K, and solution absorption spectra. The probe should be quite useful for characterizing and quantifying various inorganic and organic components on site in various environmental samples such as waste storage tanks, containers of unknown liquids, wells, soils, and groundwater. Normal Raman measurements would be applied to a high concentration of analytes; surface enhanced Raman spectroscopy (SERS) modified spectroelectrochemical SERS, fluorescence, and

classical spectroelectrochemistry would be applied to trace concentrations of components. This probe will be quite useful for both the cleanup and compliance thrusts of SERDP.

The probe essentially has the physical properties of a pure silica glass rod so can be used over the temperature range of solid SiO_2, 0 to > 1500K; it is relatively inert to many chemical environments; it is made of very pure SiO_2 and has good stability to radiation effects. It is rugged, cheap to fabricate, and can be considered to be disposable if the need arises. In the case of our molten salt Raman application, it is slowly corroded by the melt, but continues to give reliable concentration information because of the normalization procedure that we developed. We wish to build on the above studies and develop applications of this probe to the identification and quantification of contaminants at locations of interest to DOE such as waste storage tanks, wells, containers of unknown liquids or solids, streams, groundwaters, or soils.

The probe will be applied to the characterization and quantification of solution and solid contents of the waste tanks at Hanford and INEL. The anion components of these tanks, $CO_3^{=}$, NO_3^{-}, NO_2^{-}, $PO_4^{=}$, ferri- or ferrocyanides, etc., have identifiable Raman peaks. The probe should be stable to the radiation fields in these tanks because it is essentially a quartz rod.

We have applied the probe to several different kinds of spectroscopies (i.e., Raman, fluorescence, absorption and reflectance) have fabricated and considered a number of different probe-head embodiments, and have demonstrated the usefulness of various coatings on the probe head to enhance its performance. Some of these studies have been published; some are as yet unpublished. Further characterization and development in these areas will maximize the usefulness of this probe as the analytical transducer for a portable field analytical instrument. For example, fluorescence measurements using the probe will be utilized to determine amenable organic and inorganic species at trace levels in various samples at DOE sites.

The fabrication of the probe head currently involves flame fusing the optical fibers into a quartz tube under vacuum conditions. The sealed end is cut and polished after fusing to make the probe head. The fusion process needs to be evaluated in terms of optimum conditions to provide a consistent method which produces proper sealing and minimal optical "cross-talk" across fibers in the head in order to guarantee quality control in preparing the head. There are various geometrical head configurations that will improve the probe efficiency. Some are uniquely possible because of the fused head design (invention disclosure ESID 947-X). Other embodiments will be developed (invention disclosure ESID 1389X) that will permit the capabilities of focusing exciting radiation and providing for the collection of a signal at a location away from the fiber head. One could therefore characterize the contents of bottles of unknown liquids at DOE sites.

We have demonstrated that a metal-coated optical fiber can be included in the bundles of fibers to be sealed in a probe. The metal coating on the fiber has served as an electrode to carry out spectroelectrochemistry. In this context, I am referring to studies in which a chromophore is generated or destroyed electrochemically at a location where it can be followed spectrophotometrically. These changes can be followed by fluorescence, Raman, or absorption spectroscopy depending on sample. The technique carried out in this fashion is very sensitive, and we wish to apply it to environmental samples. There are other spectroelectrochemical probes based on the principle that a silver surface can be electrochemically treated to yield, at least, generic selectivity to certain organic chloride compounds over other organic compounds. It is accomplished by placing a silver electrode close to the probe. A silver coated fused glass

probe (probably with an inverted cone head) will be tested for such spectroelectrochemical SERS application. This design may greatly enhance the usefulness of an already useful environmental characterization device because the silver surface is immediately adjacent to the exciting and collection fibers.

We have carried out preliminary studies in which the all-silica fiberoptic probe head is coated with silica sol-gels. After curing the applied sol-gel, one has a porous surface on the probe head. Depending on the desired use, this surface can be clear or light scattering. Materials impregnated into the sol-gel are fixed in the sol-gel but able to interact with solutions surrounding the probe because the sol-gel surface remains porous. We have seen SERS effects by impregnating the sol-gel with silver, seen acid-base color changes by impregnated indicators, studied and published a spectral study of "buckyballs" impregnated in a sol-gel. These ideas will be further developed for their analytical usefulness.

The probe has been used to characterize, and quantify, amenable rare earth ions absorbed on the inorganic ion exchangers developed in the Chemical Technology Division at ORNL. We have done this by placing the probe in a bottle of either ZrO_2 or $Zr_3(PO_4)_4$ ion exchange beads on which Tb or Er have been absorbed. This approach is simple enough, and possibly not unique to our probe design. We want to extend the analytical usefulness of this technique so that it will be possible to analyze one or a few beads containing absorbed analytes of interest. Although we have no experience with this device for in-situ analysis, this would be possible and will be investigated. In either case this analytical approach would be applied to the identification and determination of amenable ions in bodies of water, tanks, waste streams, wells, etc.

We will collaborate with EIC Laboratories, Inc., Norwood, MA, in coupling our fiberoptic device to portable spectrometers and detectors they have developed. They have much site experience in environmental areas, and mutual interests will be served in a cooperative study. They are aware of our desires, and we have had much informal contact with them. To prepare for this collaborative effort, we require capital funds to purchase a research type spectrophotometer, CCD detector and associated computer controller to carry out laboratory studies that can be applied to their types of portable systems. One of our first demonstrations will be the use of an all-silica fiberoptic probe with EIC instrumentation for the Raman spectral characterization of components amenable to Raman spectral characterization at the Oak Ridge site.

8. Expected Payoff:

With successful completion of our project goals we will have a monitoring device that will have relatively excellent radiation and chemical stability and will be useful for many spectroscopic applications (Raman, fluorescence, SERS, absorption or reflectance). Compared with other probes which are used for such analysis, this probe should offer distinct advantages in harsh environments. It will also be simple, economical, and disposable if necessary. Already the probe is used for determining Mg ions in an industrial molten salt. After the developments described here, it shall find many other industrial applications, such as in areas of high pressure, low or high temperature, etc.

9. Milestones:

(Assuming a start date of 1/94)

1.	Probe fabrication reliability studies.	6/94
2.	Initial Raman demonstrations; Oak Ridge wells.	8/94
3.	Demonstration of Raman capabilities; Hanford, INEL, ORNL.	5/95
4.	Final head embodiment studies (geometry, electrochemical SERS, fluorescence, sol-gel indicators).	12/95
5.	Final field tests of all probes.	9/96

10. Transition Plan:

As mentioned before, EIC Laboratories, Inc. will be an active collaborator in our studies. They have contractual obligations in place with many of the DOE problem sites. Implementation of our probes will be through this connection. We have had and continue to have additional informal contact with personnel at Hanford and at LANL for use of our probes. A prototype probe is already in use at LANL and will be used for Pu Raman studies in molten salts. By means of various programs within DoD and DOE, the end results of this project will be utilized. CRADA's also will be developed for environmental and industrial users.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	435	300	225	0	960

12. Performers:

Along with the PI, there will be interactions with the Chemistry Department at University of Tennessee, Knoxville, and a retired Raman consultant in Oak Ridge. All of the above were actively involved in the Mg sensor project through which the all-silica probe was developed. We have many decades of experience in the areas of research described and together have >500 publications in this or related fields. Personnel at LANL, INEL, and Hanford will also be involved. Lastly, a cooperative development agreement of some sort will be arranged with EIC Laboratories, Inc., of Norwood, MA.

13. Principal Investigator:

Jack P. Young
Oak Ridge National Laboratory
P. O. Box 2008, MS-6142
Oak Ridge, Tennessee 37831-6142
TEL: 615 574-4922
FAX: 615-574-8363

14. Keywords:

Fiberoptic probe, Raman, radiation resistant, chemically resistant, fluorescence, contaminants

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Subsurface Gas Flowmeter

3. **Agency:** DOE

4. **Laboratory:** Sandia National Laboratories

5. **Proposal ID:** #404

6. **Problem Statement:**

In situ air stripping is a process for removing volatile organic compounds (VOC's) from the subsurface which is currently enjoying widespread use in the environmental restoration industry. Air stripping involves injecting and/or extracting air from the subsurface through vertical or horizontal wells penetrating the contaminated horizons. The flow of air through the subsurface results in the VOC's being volatilized and removed from the ground by the flowing air. In assessing the effectiveness, efficiency and zone of influence of this technology it is important to understand the dynamics of the gas flow in the subsurface. In a perfectly isotropic, homogeneous medium the gas would travel uniformly through the ground. In the real world, however, the transport properties of the subsurface are decidedly inhomogeneous, with the result that the gas travels along preferred, high permeability pathways. To properly evaluate the remediation process, one needs to delineate these pathways and define how broad and diffuse or narrow and constricted they are. Another important consideration when gas is being injected and/or extracted from the subsurface is the amount of interaction between the gas in the pore spaces in the vadose zone and atmospheric air. These effects have not been adequately investigated because of the difficulties involved in directly measuring air flux in soil. In this technology demonstration proposal it is proposed to develop a gas flowmeter which will address these needs by providing the capability to directly measure gas flow velocities in the subsurface.

The gas flowmeter being proposed is a new project that represents an extension of a technology called the In Situ Permeable Flow Sensor which has been developed by the PI with funding from DOE's Office of Technology Development. The In Situ Permeable Flow Sensor, which measures the full 3 dimensional groundwater flow velocity at a point in a saturated permeable material, was field demonstrated during the VOC Non-Arid Integrated Demonstration at the Savannah River Site and has recently been licensed to a private company which plans to commercialize the technology. The new gas flowmeter, while similar in many respects to the previously developed In Situ Permeable Flow Sensor, differs in several important aspects.

7. **Project Description:**

Both the existing groundwater flow sensor and the proposed gas flowmeter are based on the principle that the temperature distribution on the surface of a finite length, heated cylinder buried in a permeable flow field is related to the flow velocity of fluid past the cylinder. When there is no flow past the cylinder, the temperature distribution on the surface of the cylinder is independent of azimuth and symmetric about the vertical midpoint of the cylinder. In a flow

field with a significant vertical component, the vertical temperature distribution will become skewed in the direction of the flow as some of the heat emanating from the cylinder is advected along the length of the cylinder by the moving fluid. In a flow field with a significant horizontal component, the azimuthal temperature distribution will no longer be independent of azimuth. The downstream side of the cylinder will be relatively warm compared to the upstream side.

The key to implementing this basic operating principle is to ensure that the heat flux from the surface of the probe is outwardly directed with as little heat transfer occurring through the interior of the rod as possible. To accomplish this, the proposed gas flowmeter, like the groundwater flow sensor, will consist of a cylinder of low thermal conductivity polyurethane foam 75 cm long and 5 cm in diameter on the surface of which is mounted a thin film flex circuit style heater and an array of 30 temperature sensors. This assembly is then encased in a waterproof seal.

The most significant difference between measuring groundwater and gas flow with this technology will be the method used to deploy the instrument. The groundwater flow sensor is emplaced by drilling down to the desired depth using a hollow stem auger, lowering the probe down the center of the auger and then retracting the auger, leaving the probe at the bottom of the hole. In unconsolidated, saturated soils, the formation quickly collapses around the probe, leaving it permanently buried in the ground. This technique will not be appropriate for measuring gas flow, in part because unsaturated sediments do not collapse as readily as saturated sediments, but primarily because the technique introduces too large a disturbance in the formation gas permeability. Instead, the gas flowmeter will be deployed directly in a borehole where it will be capable of measuring either the vertical gas flow within the hole or the horizontal component of the formation gas flow velocity, depending on how the borehole is completed.

To measure the horizontal component of the formation gas flow, the probe will be deployed along the axis of the hole within a screened interval of the borehole and the borehole will be packed off above and below the screened interval. The diameter of the probe will be smaller than the inner diameter of the borehole so that there will be an annulus of open space between the outer surface of the probe and the inner wall of the borehole. If there is any gas flow in the formation then air will enter the borehole on one side of the screened hole, impinge upon the surface of the probe, flow around the probe and exit the hole on the opposite side from where it entered. Relatively cool temperatures would be observed on the upstream side of the probe and warm temperatures on the downstream side as some of the heat emanating from the probe is advected around the probe by the flowing air.

The same probe could also be used to measure vertical gas flow within screened or uncased holes. This type of measurement would be very useful for determining the relative permeability of different layers intersected by a borehole. If the borehole were logged as air was being pumped into or out of the hole, either artificially with a pump or naturally by a change in barometric pressure, layers of the formation with relatively high permeability would be characterized by high gradients in the vertical gas flow. Characterization of the gas flow field in the subsurface would be very useful to environmental engineers and regulators trying to understand the dynamics of natural and induced air stripping waste remediation processes and the fate and transport of contaminants in the unsaturated zone.

For both the groundwater flow sensor and the proposed gas flowmeter the direction of the fluid velocity vector can be determined very easily by analyzing the pattern of the temperature distribution on the surface of the probe. Determining the magnitude of the fluid velocity vector is more difficult. The mathematical expression which relates the magnitude of the temperature distribution on the probe to the magnitude of the fluid velocity past the probe assumes that the probe is deployed in intimate contact with an infinite, homogeneous medium. This expression cannot be used when the probe is deployed in a borehole because this assumption is grossly violated in the borehole environment. As a result, the gas flowmeter will be calibrated in a simulated borehole under conditions of known gas flow velocity. The most significant technical hurdle to be overcome is to determine the degree to which the casing material, screen size, thermal and pneumatic properties of the formation, and other factors, influence the response of the instrument. Preliminary estimates suggest that the probes should be quite sensitive to gas flow velocities as low as on the order of 0.1 ft/min. This represents a significant improvement over current technology.

The method by which formation gas flow velocity is currently measured is to deploy an array of pressure transducers at different points in the formation to determine the pressure gradient at the point of interest. The product of the pressure gradient and gas permeability of the soil yields the gas flow velocity. The problem is that the gas permeability of soils is very difficult to determine with any degree of accuracy. The PI is unaware of any other techniques for direct measurement of gas flow velocity in the subsurface. The current technique for measuring gas flow into or out of a borehole involves attaching a mass flow meter to the top of the hole and measuring the integrated flux across the entire screened interval of the hole. The gas flow meter being proposed has the advantage that it can also indicate which horizons penetrated by the hole are yielding or absorbing the most gas. These types of measurements are currently made with impeller type flow meters which are not nearly as sensitive as the proposed flow meter.

The first task will be to conduct laboratory studies in simulated boreholes to develop calibration procedures and to determine the sensitivity of the proposed technology to both vertical and horizontal gas flows. The second task will be to test the probes in a real borehole and finally to deploy them at an actual waste site where in situ air stripping is being used to remediate the contaminant. Personnel from the Hanford Environmental Restoration Department have expressed a strong interest in this technology and have offered their site as a potential field test location.

8. Expected Payoff:

The technology has the potential to dramatically improve our understanding of the dynamics of air stripping waste remediation activities, an extremely important technology currently being used extensively, both by government and private industry, to remediate hazardous waste sites. The availability of the gas flowmeter technology will improve the cost effectiveness of air stripping projects by providing information about the zone of influence of the process at a given site, thereby alleviating the necessity of conducting overly conservative cleanup sweeps. At sites where nutrients intended to enhance bioremediation of the contaminant are being delivered into the subsurface by gas injection, this technology can yield information migration paths of the injected nutrients in the subsurface.

9. Milestones:

1.	Complete lab studies and sensitivity analysis	12/31/94
2.	Complete and document calibration procedures	5/31/95
3.	Deploy instruments at a hazardous waste site	8/31/95
4.	Complete data collection	12/31/95
5.	Complete final report on technology	3/31/96

10. Transition Plan:

By the completion of the work described in this proposal, the technology will have been developed to the point of commercial viability and have been tested and demonstrated at an actual waste site. As the technology is being developed, industrial partners interested in commercializing the technology will be actively sought. S. I. E., Inc. of Fort Worth, Texas, the company which is currently commercializing the In Situ Permeable Flow Sensor, has expressed an interest in participating in the development of this technology and in commercializing it, if it proves marketable. A letter from S. I. E., Inc., stating their interest in this project is attached.

The ultimate users of this technology will be Environmental Restoration Departments at the various DoD and DOE facilities around the country as well as private industries. Discussions with ER representatives at the DOE Hanford Site have been very encouraging. They expressed a strong interest in using the technology once developed and offered their site as a possible field test location.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	125	250	125	500

12. Performers:

The work described in this proposal will be carried out by the Principal Investigator, a Senior Member of Technical Staff at Sandia National Laboratories. As mentioned above, S. I. E., Inc., has expressed an interest in participating in the development of this technology. If this project goes forward, the option of concluding a CRADA with them will be vigorously pursued very early in the project.

13. Principal Investigator:

Sanford Ballard
Geophysics Department, 6116 (Mail Stop 0750)
Sandia National Laboratories, Albuquerque, NM 87185-0750
Tel (505) 844-6293 FAX (505) 844-7354 email: sballar@ca.sandia.gov

14. Keywords:

Gas, flow, flowmeter, air-stripping, bioremediation, vadose.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation

3. **Agency:** USEPA

4. **Laboratory:** Risk Reduction Engineering Laboratory

5. **Proposal ID:** #371

6. Problem Statement:

Petroleum hydrocarbons, and other volatile organic compounds (VOCs), which are found to contaminate groundwater and soils, are usually treated by pump-and-treat methods, which are very time-consuming, expensive, and not very effective. We are proposing the use of pervaporation for effectively removing these hydrocarbons and VOCs from contaminated soil and groundwater (with or without using surfactants) and concentrating them by at least a thousand-fold, for economical disposal or recycle/reuse using specially designed hydrophobic membranes.

7. Project Description:

Petroleum hydrocarbons and other volatile organic compounds (together described hereafter as VOCs) from various industrial activities in both civilian and military sectors are frequently found to contaminate groundwater and soils. These VOCs typically are transportation fuels, and solvents including chlorinated organic compounds such as trichloroethylene (TCE), carbon tetrachloride, tetrachloroethane (PCA). Many of these VOCs are potential carcinogens. In groundwater the VOCs exist as non-aqueous phase liquid pools (NAPLs), which are of two types, light NAPL (LNAPL) which floats on water, and dense NAPL (DNAPL) which sinks under water. The NAPL pools are a long-term source of contamination, as the organics slowly leaks into the aquifer water, which then is unusable for human use, and if the water discharges into a river or a lake, it poses danger to aquatic life. Soil contamination by VOC is a source for continuous air pollution and is also a source for groundwater pollution.

The technology of choice for remediating these environmental problems is the so-called pump-and-treat method, one variation of which is circulating water through the contamination area and pumping it out to a treatment stage, typically carbon adsorption, which needs to be subsequently regenerated, and the VOCs disposed of chemically. We propose to develop a simpler and more effective technology which will use the membrane pervaporation method. This method removes the VOCs from the water and concentrates it by at least a thousand-fold, which permits much more economical recovery for recycle/reuse.

In the "pump" part of the pump-and-treat process, the use of surfactants has been proposed for enhancing the removal of VOCs from the groundwater or soil matrix (surfactant flushing). While the VOCs will indeed be removed more efficiently by emulsification, the oil-water emulsion is harder to dispose of by ordinary means of bioremediation or carbon adsorption. We

are proposing pervaporation as a means of breaking the emulsion while removing the VOCs from the contaminated water. The efficiency of pervaporation for VOC removal from water has already been demonstrated in several studies to be better then 99%. The use of pervaporation for breaking oil-water emulsions is protected by an invention disclosure at RREL-EPA.

Pervaporation works on the principle of solution diffusion, i.e. the organic compounds dissolves in the non-porous membrane, diffuses out to the permeation side, and evaporates. The energy for this evaporation is conveniently provided with the feed stream itself. In contrast to conventional membrane processes, which use porous membranes, pervaporation membranes are not akin to filtration, and are therefore less prone to mechanical fouling. For VOCs, which are hydrophobic, a hydrophobic membrane is appropriate. Either a vacuum or an inert sweep gas is employed on the permeate side of the membrane. Usually the VOCs permeate through a hydrophobic membrane, such as one made of polydimethylsiloxane or silicone, orders of magnitude faster than water, as a result of which the VOCs are highly concentrated. For instance, it is possible to concentrate a 100 ppm VOC-solution to over 10% VOC solution (or suspension).

The composition and morphology of the membranes are a key to effective use of pervaporation technology. It is best to use a thin film of the discriminating layer deposited on a highly porous support structure. In addition, RREL-EPA has invented specially doped membranes that enhance the selectivity by 40% or more. An invention disclosure has also been made on the use of these membranes for pervaporation.

The proposed research has four parts:

1. Use of special membranes: These membranes will be designed, fabricated and tested for their superior VOC-selectivity and transport rates.

2. Bench-scale test: Laboratory research will be conducted to investigate the removal of VOCs from simulated ground water and surfactant-flushed VOC-solutions. Transport rates, selectivity, and separation factors will be measured.

3. Mathematical modeling will be conducted to predict the design features of a prototype for a designated removal efficiency. This is a mere extension of modeling currently being done at RREL in cooperation with the University of Cincinnati.

4. We will collaborate with a membrane company, such as Membrane Technology and Research (MTR, Inc.), Palo Alto, California, for a pilot demonstration of VOC-removal from contaminated water (with or without surfactant in it). MTR, Inc. specializes in pervaporation research and has tested several pilot modules for removing VOCs and CFCs from air and water streams. We propose to demonstrate the technology at a defense facility.

All work from proof-of-concept of the removal of VOCs from VOC-emulsion in water to pilot demonstration can be completed in two years from the inception of the study.

8. Expected Payoff:

The proposed technology will make two specific advances: (1) provide a cost-effective way of dealing with surfactant-VOC solutions, and (2) provide a boost to the use of surfactants for

groundwater and soil remediation. Large savings will accrue from this practical and efficient technology.

9. Milestones:

End of Year 1: Selection and fabrication of special membranes. Completion of laboratory measurements of flux and separation factors for VOCs, and model prediction of module design for pilot demonstration.

End of Year 2: Completion of pilot demonstration. Documentation of the benefits of the technology.

10. Transition Plan:

The pilot demonstration at a defense site will constitute technology transfer to DoD.

11. Funding: ($K)

	FY94	FY95	TOTAL
SERDP	280	500	780

RREL will complement the proposed program with $60K already earmarked in FY'94 for the in-house study. The in-house study, which is currently focused on fundamentals, will be redirected to this high priority research.

12. Performers:

The first three parts of the delineated research will be conducted in-house at RREL-EPA. The demonstration will be conducted under contract by a membrane company based on the model prediction and laboratory results.

The Naval Facilities Engineering Science Center (NFESC), will collaborate with us in all phases of this work. Point of contact: Ms. Leslie Karr, Code 411, NFESC, Port Hueneme, CA 93043, Tel: 805-982-1618. The Airforce's Armstrong Laboratory Environics Directorate was contacted (Capt. Mark Smith, Tel: 904-283-6126). They will be interested in demonstrating the technology at an appropriate Air Force facility, if it is shown to be cost-effective.

13. Principal Investigator:

Dr. Subhas K. Sikdar, Director
Water and Hazardous Waste Treatment Research Division
Risk Reduction Engineering Laboratory
Cincinnati, OH
Tel: 513-569-7528
Fax: 513-569-7787

14. Keywords:

Emulsion, surfactant, pump-and-treat, pervaporation, membrane.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Areas:** Cleanup
2. **Title:** Subsurface Bioremediation Process Monitoring Indicators
3. **Agency:** EPA
4. **Laboratory:** RSKERL
5. **Proposal ID:** #383
6. **Problem Statement:**

The application of in-situ, active or passive bioremediation of fossil fuel contamination holds promise of achieving both detoxification and source removal of regulated compounds such as BTEX (i.e. benzene, toluene, ethylbenzene and xylene). BTEX as well as other mobile constituents of fuels and solvents are a major category of subsurface contaminant mixtures present at DoD installations. These contaminant mixtures entered the subsurface as a result of spills or releases from fuel tanks, pipelines, maintenance areas, and fire-training installations. The scope of known problems, in a variety of hydrogeologic settings, requires a systematic, cost-effective approach to monitoring the progress of bioremediation processes and plume transport. In most cases, methods applied to the detection or assessment of specific subsurface contaminant distributions in aqueous or solid matrices have been applied to long-term monitoring during remedial action operations. However, disappearance of source-related compounds from ground water alone is insufficient evidence for removal. Reliable indicators of the progress of bioremediation actions, including the monitoring of metabolic intermediates in aquifer solids and water are needed in order to evaluate the performance of remediation schemes and to complement source contaminant monitoring efforts. (National Research Council, In-Situ Bioremediation When Does It Work?, National Academy Press, 1993.)

The major problem we intend to address is the need to identify biochemical pathway metabolites and critical substrates so that engineered mass-balances can be approached. In this way it may be possible to link net contaminant destruction or transformation to both hydrogeochemical conditions and specific biodegradation pathways. With this process level understanding, we should be able to more easily apply bioremediation to other sites. Acceptance of passive or "low-technology" bioremediation schemes can be achieved when mass-balances and definable endpoints for contaminant removal are achieved.

The needs for these monitoring improvements are recognized in several SERDP Thrust Areas: 1.B: Site Characterization and Analysis Penetrometer System, 1.III.1.e. Improved Standards and Analytical Techniques for Defining "Clean"; 1.C: Characterization/Monitoring, 1.III.3.a. Improved Subsurface Condition Description and Simulation; 1.D: Chemical Analytical Systems, 1.III.1.o. Improved Chemical Analysis Technology for Finger-Printing Organic Contaminants; 1.J: Treatment of Fuels in Groundwater, 1.I.1.e. Process to remediate Groundwater Contaminated with Hydrocarbon Fuels; and 1.T: Bioassay/Biomonitoring Methods; 1.III.1.j. Long-term, In-place Monitoring of Remediation Effectiveness and 2.II.2.e. Improved Biomonitoring Capability.

The specific applied research needs addressed by this project are: (1) the correspondence between apparent oxidation-reduction and hydrogeochemical conditions with major organic metabolite concentration distributions in source, transitional and downgradient zones, (2) the identification of mass distributions (i.e. including solid-associated and aqueous) of the principal electron acceptors, metabolites of regulated compounds and potential organic substrates present in the media (e.g. microbially derived: such as, acetate, formate, etc., and background organics, fatty acids, hydrocarbons and fire-fighting foam constituents), and (3) the temporal and spatial variability in: critical geochemical indicators (e.g. O_2, NO_3^-, NO_2^-, NH_3, Fe_{Total}, Fe^{2+}, Mn_{Total}, Mn_{Diss}, CO_2, CH_2 and CH_4) and major metabolites (e.g. formate, acetate, propionate,......as well as, benzoic, toluic, salicylic acids and isomers).

This applied research project builds on the basic work begun with USEPA-RSKERL support (Barcelona, Tomczak, Lu & Virkhaus, Petroleum Hydrocarbons in the Subsurface Conf, In-Press, 1993) which had the general goal of redox-specific characterization of organic matter in both contaminated and uncontaminated aquifers. In this work, major fractions of soluble organic matter and acidic metabolites from the microbial decomposition of hydrocarbon fuels were determined. It showed the importance of hydrogeologic and oxidation-reduction (i.e. redox) potential control over major transformation pathways and that significant degradation of fuel constituents occurs even under anoxic or reducing conditions. The methods developed in this work and that of Cozzarelli et al. (Geochimica Cosmochimic Acta, In-Press, 1993; Environ. Geol. Wat. Sci., 16, 293-297, 1990) are directly applicable to monitoring the progress of microbial processes which occur under a variety of subsurface remediation measures (e.g. air sparging, bioventing, solvent or surfactant flushing). The project's emphasis on both inorganic and organic indicators of bioremediation will aid in the definition of cleanup benchmarks and endpoints. It directly addresses the approach to answering the question of "how clean is clean"?

7. Project Description:

The overall goal of the project is to determine those hydrogeochemical conditions under which hydrocarbon fuels can be degraded in the subsurface with an emphasis on: major transformation conditions and pathways, mass distributions of both source-related compounds and metabolic products, and the spatial and temporal variability in these distributions which bear on the extent of bioremediation efficiency. It directly relates to the Cleanup Thrust Area's R & D objectives which aim at both verifiable and cost-effective site investigation, characterization and remediation technologies.

Objectives. The objectives of the work include: (1) Hydrogeochemical Zonation: Determination of the correspondence between redox and hydrogeochemical zones of the subsurface with loci of microbial transformation, (2) Contaminant Distributions: Determination of the fractionation of critical inorganic and organic transformation indicators in water and aquifer solids, and (3) Spatial and Temporal Variability: Determinations of the variability in the mass distributions to evaluate techniques for volumetric averaging and performance criteria for bioremediation operations. The project has been designed to be conducted in parallel with either operational or experimental remediation efforts at sites where hydrocarbon fuels constitute a contamination problem. As such, the project can be conducted at any of a number of DoD or DoE installations where access can be assured. The Wurtsmith AFB, Oscoda, MI, would be an excellent candidate site given our familiarity with the hydrologic setting, hydrogeochemistry and the focus on bioremediation at the site. It represents a "fast" site characterized by potentially high fluxes of both nutrients and water, as well as high hydraulic conductivity which facilitate high

biodegradation rates and potential options for engineered enhancements (Hickman et al. J.W.P.C.F. 61, 9, 1564-1575, 1989).

Technical Approach. The three main objectives of the project will be approached in a phased manner building on the existing array of monitoring points and initial site data review. Overall scheduling is flexible based on a FY94 or FY95 start.

Phase 1. Initial Reconnaissance and Delineation of Hydrogeochemical Zones. The existing array of monitoring wells will be sampled and preliminary borings will be made taking water and solid samples at alternate depths for the initial delineation of redox-zones. Field analyses will include: O_2, temperature, pH, conductance, Fe^{2+}, NO_3^-, NH_4^+, alkalinity, CH_4, CO_2, and volatile organic compounds (VOC's). Solid and H_2O samples will be returned to the lab for determination of: total VOC's, inorganic and organic carbon, extractible acid metabolites and intermediates, non-volatile organic compounds (e.g. hydrocarbons, fatty acids, surfactants, fire-fighting foam agent), total Fe and Mn. Appropriate microcosm experiments will be run to evaluate biological activity in selected redox zones. On the basis of these results the initial hydrogeochemical zones and loci of bioactivity will be located and geostatistical estimations of sources and downgradient plume composition will be done. Selected areas for supplemental borings will be determined to expand the biomonitoring array in Phase 2.

Phase 2. Development of Optimized Biomonitoring Network and Long-Term Microcosm Experiments. The geostatistically (kriging) based distributions of redox/hydrogeochemical zones and loci of bioactivity include levels of confidence in estimating concentrations between known points. Supplemental borings and water sampling points will be located to reduce uncertainty within regions of the subsurface and the field and lab work in Phase 1 will be repeated with improved resolution. Refined estimates of background conditions and total contaminant mass per unit volume of aquifer will be developed and the network will be optimized (i.e. minimizing uncertainty) for the evaluation of spatial and temporal variability in critical indicators of contaminant removal. The approximate rates of biotransformation of the principal contaminants from microcosm experiments will be evaluated with respect to increases in metabolic products and correlated with the distributions found in the field.

Phase 3. Evaluation of Variability and Net Bioremediation Over Time. The network will be sampled at intervals (e.g. quarterly) to evaluate temporal and spatial variability in redox/hydrogeochemical zonation and progress of contaminant removal/metabolite production. It is anticipated that the methods we have used in past work (Barcelona et al., Environ. Sci. and Technol. 25, 5, 991-1003, 1989) will serve to control sampling and analytical error so that actual subsurface variability can be determined at known levels of confidence. Seasonal effects on nutrient supply, dispersion and transport will be evaluated at selected intervals simulating the field results with stepwise applications of two-dimensional flow and transport models. It is likely that at least eight quarters of data collection will be needed to evaluate these effects. Borings will be taken and characterized as before to benchmark the progress of bioremediation and estimate timeframes for net contaminant removal.

8. Expected Payoff:

The results of the work will provide a conceptual model for the design and operation of cost-effective remediation efforts. Minimizing the number of wells/borings at such sites and uncertainties in contaminant distributions while providing known levels of confidence in net

contaminant removal will reduce the life-cycle costs of remediation efforts. Also, definable benchmarks for evaluating the performance of remediation efforts will serve to better allocate fiscal and human resources at DoD and DoE installations.

9. Milestones:

Phase 1

a.	Initiate Site Data Review and Planning	09/94
b.	Initiate Reconnaissance (borings, water sampling/microcosm setup)	12/94
c.	Delineation of Hydrogeochemical Zones	6/95
d.	Correspondence Between loci of Bioactivity and Hydrogeochemical Zone	9/95
e.	Geostatistical Averaging and Net Contaminant/Metabolite Distribution	3/96

Phase 2

a.	Supplemental Borings/Water Sampling/Microcosms	6/96
b.	Estimation of Bioremediation Rates	9/96
c.	Geostatistical Refinement of Network	12/96
d.	Initiate Quarterly Sampling	3/96
e.	Preliminary 2-Dimensional Modeling	6/96

Phase 3

a.	Continued Quarterly Sampling	6/96-3/98
b.	Complete refined estimates of mass removal	3/97, 3/98
c.	Complete conceptual Model Development	9/97-3/98

10. Transition Plan:

In addition to peer-reviewed papers and reports which will issue from the project it is clear that technology transfer must occur within DoD, DoE and the environmental restoration community. Public presentation at conferences, short-courses, and workshops which we support will be enriched in the future by the results of the project. We would welcome the opportunity to offer focused short-courses for DoD and DoE personnel as well as contractors to broaden the communication of results. It is likely that a pilot course could be offered at the experimental site(s) during the project period if logistics can be arranged. A two-day monitoring short-course with field exercises has been budgeted for Year 2 of the work (FY96). The pilot course could be made part of the project review process involving DoD or DoE project officers, AFIT staff and others as participants.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	550	575	595	615	2335

12. Performers:

Dr. Candida West of the USEPA-RSKERL will be the project manager and provide overall direction of the laboratory work on non-volatile organic compounds and microcosm studies. Dr. West's current research activities include identification of dissolved and solid-associated organic carbon compounds associated with sorption and biodegradative processes. The participation of faculty and graduate students from the host institution of Dr. Michael Barcelona will be key to the project. Dr. Barcelona has worked with both the USEPA-RSKERL and EMSL-Las Vegas laboratories for the past thirteen years, bringing considerable benefit to the field of groundwater contaminant monitoring and subsurface geochemistry during this period.

13. Principal Investigator:

Dr. Candida C. West
USEPA-RSKERL
P.O. Box 1198
Ada, OK, 74820
405-436-8551; (FAX) 405-436-8529

14. Keywords:

Subsurface remediation, bioremediation, monitoring network design, geostatistics, cleanup endpoints, contaminant transformation.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** In-Situ "INSIDE-OUT" NMR Sensor for Contaminant ID

3. **Agency:** Department of Defense : Navy

4. **Laboratory:** Naval Command, Control and Ocean Surveillance Center
RDT&E Division - San Diego, CA

5. **Proposal ID:** #038

6. **Problem Statement:**

Determination of the feasibility for the adaptation of the emerging "INSIDE-OUT" Nuclear Magnetic Resonance (NMR) technique of compound identification to rapid site screening of hazardous waste sites. Recent developments in the area of high energy density magnets (rare earth and high temperature superconducting magnets) will allow for a significant reduction in the physical size of this type of sensor. This technique allows a well defined volume of soil surrounding the sensor to be analyzed without collection of samples.

7. **Project Description:**

The concept of reversing the locations of the sample and the source of the magnetic fields required to Nuclear Magnetic Resonance Spectroscopy was proposed and verified by Jackson, Burnett and Harmon[1] for the Department of Energy, Los Alamos Scientific Laboratory in 1980. The technique developed produces a region of homogeneous magnetic field external to the apparatus. A coaxial nuclear magnetic resonance coil is periodically pulsed at radio frequencies to briefly produce a toroidal magnetic field at 90° to the steady homogeneous field. If the frequency of the rf magnetic field is adjusted to synchronize or "resonate" with the Larmor frequency of precession of the nuclei present in steady magnetic field and realign the direction of their nuclear magnetization vector accordingly. The intersection of the steady homogeneous magnetic field and the toroidal rf magnetic field define the "sensitive sample volume". With the cessation of the rf magnetic pulse, the realigned or "flipped" nuclei will start to precess due to the Earth's magnetic field. The coupling between the precessing magnetization vector and the NMR coil allows the NMR free-induction decay (FID) signal to be detected. The amplitude of the signal is related to the number of nuclei present, and the rate of signal decay is related to the local environment of the nuclei, i.e., the chemical bonds to other near by atoms.

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[1]J.A. Jackson, L.J. Burnett, and J.F. Harmon, "Remote (Inside-Out) NMR. III. Detection of Nuclear Magnetic Resonance in a Remotely Produce Region of Homogeneous Magnetic Field", *Journal of Magnetic Resonance,* 41, 411-421, (1980).

Jackson[2] has demonstrated the variation of the radial magnetic field (H_r) vs. radial distance r, as a fraction of the axial magnetic field (H_0) at the center of an isolated magnet. With a h/a value of 3, where h is the axial distance from the pole face to the midplane and a is the radius of the pole face respectively, the radial magnetic field is very uniform for the region defined by the ratio r/a between the values of 1.9 - 2.8.

The Larmor frequency of the precessing magnetization is given by: $B = B_p\cos(w_0t)$ where: B_p is the value of the radial magnetic field in the region discussed above, w_0 is the Larmor frequency, and t is time. If the quantity g is referred to as the relative signal per unit volume of toroidal sample, referenced to a known coaxial sample of volume V_r, then g can be expressed as $g \equiv (I_s/V_s) \,/\, (I_r/V_r)$ [1]
where I is signal amplitude and V is the volume of material involved, and the subscripts $_s$, $_r$ and $_c$, denote the toroidal and reference samples, and the NMR resonance coil respectively.

For brevity, the following simplifications will be made: R is taken to be the average of the inner and outer radii of the toroid in the mid-plane, and R >> than the radius of the cross section of the toroid. That Faraday's law for the sample coil, with a quality factor of Q and N number of turns, can be expressed as $I = -NQA(d\phi/dt)$ with $\phi = B \cdot A$ and $B = B_p\cos w_0t$. Then, the peak value B_p for the reference sample can be expressed as $B_p = 4\pi\mu_p nf$ & $\mu_p nf = M$ where M, the magnetization, is based on the proton magnetic moment, the number density of protons, and the Boltzmann factor for the fraction of protons contributing to the net magnetization.

For the sample, only a portion of the flux is link and
$A = A_c = \pi a^2$, then $B_p = MV_s/R^3$ and
$I_s = NQA_cw_0B_p \sin w_0t = NQA_cw_0[MV_s/R^3] \sin w_0t$
so that,

$$(I_s/V_s) = NQA_cw_0[M/R^3] \sin w_0t \qquad [2]$$

Similar manipulation for the reference sample's value results in

$$(I_r/V_r) = 4\pi NQw_0M/l \sin w_0t \qquad [3]$$

where l is the length of the reference sample and $V_r = A_rl$.

Combining Eqs. [1], [2], and [3] results in the relative signal per unit volume
$g = a^2l/4R^3$

involving only geometric parameters of, or define by, the apparatus and the maximally coupled reference sample (the best instrumental signal that can be obtained).

Substitution of practical values for these parameters, as reported by Jackson[3], for the radial magnetic field in an acceptable operating configuration (r/a = 2, a = 5 cm, reference sample

[2] J.A. Jackson, "Nuclear Magnetic Resonance Well Logging", *THE LOG ANALYST*, 16 - 30, SEPTEMBER-OCTOBER, 1984.

[3] J.A. Jackson, ibid.

length ≈ 5 cm) yields a value for g = 0.05. This is in agreement with experimentally measured values of g reported by Burnett and Jackson[4] of 0.04 for this ratio of r/a. These experimental studies employed radial magnetic field of ≈ 120 G, derived from large Alnico permanent magnets, and a Larmor frequency of ≈ 500 kHz; this produced a signal-to-noise ratio (S/N) of 1:20. Much of the noise associated with these measurements resided in the electronic used to process the signals. Modern contemporary electronics and signal processing techniques should result in an improvement of the S/N ratio, and improve the operational reliability and sensitivity.

The major risk area that this proposal will investigate is the feasibility of applying contemporary magnet technology to this NMR technique and thus developing a much more compact, or miniaturized, Inside-Out NMR sensor which can be utilized with current site screening methodology (test wells), and future sensor deployment platforms, to rapidly locate, identify, and map subterranean hazardous waste deposits. With proper design the proposed sensor apparatus and calibration, such a system would be capable of accurate remote (in-situ) quantification of various subterranean chemical compounds containing hydrogen, fluorine, phosphorous, or thallium, at hazardous waste sites.

Consultation with Prof. Lowell Burnett (a nationally recognized NMR expert, and author of the works sited above) of San Diego State University and President of Quantum Magnetics, has indicated that this proposed sensor has a high probability of success for its envisioned use, particularly for high explosive compounds and petroleum based products. He has also proposed to cooperatively develop this project, manufacture and market any viable product which may evolve as part of the technology transfer effort (A letter of cooperation is attached).

8. Expected Payoff:

This detector, when fully developed, will allow for rapid and cost effective screening of proven and/or suspected sites contaminated with chemical compounds for which it has been calibrated. The ability to identify and quantify contaminants in subterranean strata behind well casings will allow the placement of a single test well, drilled and cased to the maximum investigative depth, rather than many wells which vary in depth in order to collect the necessary strata effluents. The reduction in the number of unnecessary test wells and their attendant costs in time and money, for installation, sample collection, laboratory analysis, and sample transportation, is considerable. If the number of test wells can be reduced by a factor of five (80% reduction in the number of wells), it is estimated to reduce the overall cost of this phase of site remediation approximately 40 - 50%, by accurate determination of the boundaries and depth of the contaminant plume before and after site remediation efforts.

If we conservatively estimate the cost of drilling and casing a well at $20/ft, for a 50 ft well, and disposal of the tailings, at $4,000.00; the associated required test well lifetime of analytical laboratory analysis (X samples per year for Z years as required by EPA) at $5,000.00; then the cost per well is $10,000.00. Further, assume that the time required to install a well and receive the initial laboratory analysis report (approximately 4 weeks) would not be lost. If the number of well installed per year is reduced by 500, then the monetary savings will be $5,000,000.00.

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[4]L.J. Burnett and J.A. Jackson, "Remote (Inside-Out) NMR. II. Sensitivity of NMR Detection for External Samples", *JOURNAL OF MAGNETIC RESONANCE*, 41, 406 - 410 (1980).

Also, the environmental and personnel health risks are reduced since the amount of hazardous tailings wastes generated during the drilling operations will be reduced in proportion to the number of wells drilled.

9. Milestones:

1.	Start project	06/94
2.	Complete review of applicable technologies	08/94
3.	Complete assessment of high strength permanent magnets	10/94
4.	Complete functional specifications for equipment	12/94
5.	Complete procurement & assembly of system	04/95
6.	Complete measurements of target compounds	09/95
7.	Complete assessment of feasibility	10/95
8.	Complete design & fabrication of prototype	02/96
9.	Start field trials	04/96
10.	Complete field trials & assess results	09/96
11.	Complete documentation for transition to industry	12/96

10. Transition Plan:

Under the guidance of the Technical Program Officer and Technical Program Manager, the operable system will be subject to field trials at selected DoD/DOE sites. The results of those field trials shall be reported and distributed as requested. At the conclusion of this effort the operable hardware, procured as part of this effort, shall be turned over to the identified program office within the SERDP defined lead agency. The basic technology will be transferred through the development of U.S. government patents, and through the cooperative development with the responsible industry partner, Quantum Magnetics in the United States, along with the transfer of technology previously developed from the Department of Defense as part of this effort.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	450	480	515	315	1760

12. Performers:

1. NCCOSC, RDT&E DIV, San Diego, CA (Codes 524, 754)
2. DOE : LANL
3. Quantum Magnetic; San Diego ,CA
4. San Diego State University Foundation, San Diego, CA (Contractor support and consultation with faculty)

13. Principal Investigators:

Gary Mastny & Dr. Mark North
NCCOSC RDT&E DIV 524 & 754
SAN DIEGO, CA 92152-6320
Phone: (619) 553-2802, 553-6761
FAX: (619) 553-6305

Dr. Lowell Burnett, President
Quantum Magnetics
11578 Serrento Valley Rd.
San Diego, CA 92121
(619) 481-4015

14. Keywords:

Nuclear Magnetic Resonance, Inside-Out NMR, Nuclear Magnetic Logging

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Mobile Underwater Debris Survey System (MUDSS)

3. **Agency:** Navy

4. **Laboratory:** Naval Surface Warfare Center, Dahlgren Division, Coastal Systems Station (CSS)

5. **Proposal ID:** #052

6. Problem Statement:

The goal of the MUDSS project is to demonstrate the technologies necessary for underwater surveys of shallow water inland and coastal sites littered with ordnance. A successful demonstration will prove the concept of a trailerable, low-maintenance, catamaran-based system capable of finding and mapping the locations of ordnance ranging from small shells to large bombs in water depths of from four to forty feet. MUDSS will supply the object detection and classification technology necessary for the environmental cleanup of ordnance at scores of underwater ordnance litter sites.

MUDSS is a new technology demonstration and transfer program. To solve the underwater ordnance search and mapping problem it addresses, MUDSS will marry technologies CSS has been developing over the past twenty years for similar minehunting problems with data fusion and visualization technologies developed at Jet Propulsion Laboratory (JPL) for NASA.

7. Project Description:

The technical objective of MUDSS is to demonstrate sensor and processing capabilities which enable (1) the detection and classification at underwater sites of ordnance that may be partially or fully buried in sediment, and (2) the discrimination between ordnance and false targets in the area such as rocks and seashells.

To accomplish this objective, existing acoustic, magnetic, electro-optic (EO), and chemical sensors and associated signal processing hardware and software developed for other Navy and JPL projects will be leveraged for the MUDSS application. To minimize risk, the project will proceed in two phases:

- Phase I (12 months duration) assembles a prototype MUDSS and executes a feasibility demonstration (FD) against an ordnance target field in very shallow water (VSW) at CSS.

- Phase II (24 months duration) refines the MUDSS prototype and executes a technology demonstration (TD) at multiple shallow and very shallow water (SW/VSW) sites.

CSS successfully addressed the similar problem of proud and buried bottom mine minehunting for deeper water (depths greater than thirty feet) in the late 1980's through the development of

superconducting magnetic field gradiometer and active synthetic aperture sonar technologies in the MADOM (Magnetic and Acoustic Detection of Mines) developmental program. This program culminated in a successful ATD in 1990. A large follow-on technology development effort (the Mine Reconnaissance/Hunter, or MR/H, program) is now underway at CSS to further improve the Navy's minehunting capability in very shallow water. MUDSS is very similar to MADOM and MR/H, and will leverage $8.6M of the Navy's FY 93-95 investment in MR/H.

The integration of a sophisticated field-deployable sensor suite of the kind proposed for MUDSS is a difficult technological undertaking. Cost and risk are minimized by using state-of-the-art magnetic, acoustic, and EO sensors that have already been developed by MADOM or are being developed by MR/H; by using a chemical sensor already developed at JPL; and by employing a joint CSS/JPL team experienced with these sensors.

The cost and risk of the MUDSS processing development is minimized by using a COTS (commercial off-the-shelf) hardware design for the required 2 Gflop processor similar to a design used for the MR/H processor; by taking advantage of automated classification algorithms for sonars and gradiometers developed at CSS for other programs; and by leveraging $7.0M of JPL's FY 93-95 processor hardware, automatic target recognition, sensor fusion, and 3-D visualization development programs for NASA.

The MUDSS project will have four tasks:

- Sensor suite adaptation and integration
- Automatic target recognition processor (ATRP) development
- Data fusion and visualization tools development
- Platform system development, systems engineering, and MUDSS demonstration

The task objectives and approaches are described below.

Sensor suite adaptation and integration task

The task objectives are to modify sensors that have been or are being developed by other programs and to integrate them into a sensor suite capable of:

- high resolution, multi-aspect acoustic imaging of proud or shallowly buried ordnance in SW/VSW at ranges up to 50 m
- high resolution optical imaging of proud ordnance in SW/VSW at ranges up to seven optical attenuation lengths
- multi-target magnetic localization of buried and proud ordnance at ranges up to 50 m
- short-range chemical detection of explosives

The task approach in Phase I is to:

- Assemble a prototype MUDSS sensor suite of modified and/or refurbished off-the-shelf sensors: the MADOM gradiometer (SGMS), CSS's High Performance Sidescan Sonar, the MADOM synthetic aperture sonar, the MR/H EO sensor, and the JPL mass spectrometer explosives detector (MSED).

- Collect ordnance test articles for the FD and measure their magnetic moments, acoustic target strengths, EO reflectivities, and underwater chemical signatures.
- Expand the CSS magnetics performance prediction model (MAPPS), the CSS acoustics performance prediction model (SWAT), the CSS electro-optic performance prediction model (IMPERSonator), and JPL mass spectrometer performance prediction model (MSEDM) to include the target and environmental parameters of the FD, and predict the prototype sensor suite performance.
- Validate these expanded models, or improve them as necessary, using the FD data.

The task approach in Phase II is to:

- Use the validated performance prediction models to determine modifications to the proposed MUDSS TD sensor suite. Use SWAT to design changes to the MR/H sonars to optimize SW/VSW performance against the selected ordnance target types; IMPERSonator to determine modifications to the MR/H EO sensor; MAPPS to select between SGMS and a room temperature gradiometer (RTG) being developed by a Navy Special Warfare program; and MSEDM to determine modifications to MSED.
- Modify the MR/H sonar and EO systems as necessary; refurbish the SGMS gradiometer probe, data link, and dewar if RTG is not selected; and modify MSED as necessary.

ATRP development task

The task objective is to develop a high-speed (approximately 200 Mbit/sec) ATRP for MUDSS sensor suite operation, automatic target detection and classification, and 3-D visualization of fused sensor data in a noisy and cluttered background.

The task approach in Phase I is to:

- Modify and improve existing CSS automated acoustic and magnetic target classification routines.
- Develop initial EO morphological classification routines.
- Exercise the classification routines off line against the FD data.

The task approach in Phase II is to:

- Design and build a COTS-based sensor operation system and processor.
- Develop improved classification routines and implement them on the processor for real-time operation during the TD.

Data fusion and visualization tools development task

The task objective is to develop a near real-time, dynamic, 3-D visualization capability to maximize operator understanding of the multi-sensor data.

The task approach in Phase I is to:

- Develop prototype visualization and fusion tools for the MUDSS sensor suite.
- Exercise these tools off line against the FD data.

The task approach in Phase II is to:

- Refine and expand the MUDSS visualization and fusion tools.
- Implement these tools on the ATRP for near real-time operation during the TD.

Platform system development, systems engineering, and MUDSS demonstration task

The task objectives are to:

- Develop a trailerable, low-draft, low-maintenance, single unit catamaran platform for MUDSS.
- Perform the prototype and TD system integrations.
- Execute the MUDSS feasibility and advanced technology demonstrations.

The task approach in Phase I is to:

- Procure a low-cost, commercially available, non-magnetic vessel to deploy the MUDSS prototype sensors and to house the data acquisition system.
- Plan and execute the FD.

The task approach in Phase II is to:

- Develop a specially made non-magnetic catamaran for the TD.
- Perform system integration and execute system configuration control for the TD system.
- Plan and execute the TD.

The MUDSS project is under the CLEAN-UP part of the Tri-Service Environmental R&D Strategic Plan with specific application to requirement number 1.III.2.f for improved site characterization and monitoring/sensing. No military platform is required.

8. Expected Payoff:

With its capacity to map the locations of ordnance from small shells to large bombs in all coastal or inland waters with depths between four and forty feet, MUDSS will be a capable clutter surveying system for scores of underwater ordnance litter sites. Each MUDSS sensor will out-perform any COTS sensor, and the integrated MUDSS system will provide performance against ordnance (including buried ordnance) far exceeding any COTS system. As a self-contained, easily transportable, low maintenance, and low operating cost system whose development costs have been heavily born by parallel Navy and NASA programs, MUDSS will be efficiently amortized.

9. Milestones:

Phase I (12/93 Start)

1.	Complete prototype system design	01/94
2.	Deliver all prototype system components	06/94
3.	Complete prototype system integration/checkout	09/94

4.	Execute FD	10/94
5.	Complete initial FD analysis	12/94

Phase II

1.	Complete TD system feasibility analysis/design	03/95
2.	Complete model validation on FD data	05/95
3.	Demonstrate TD processing/display on FD data	10/95
4.	Complete laboratory verification of sensor performance	12/95
5.	Deliver all TD system components	12/95
6.	Complete TD system integration/checkout	06/96
7.	Complete TD classification/clutter tests	09/96
8.	Complete TD report	12/96

10. Transition Plan:

A viable transition to a commercial capability is ensured by the early insertion of industry into the MUDSS program. CRADA's and/or procurement will be used to provide industry sensor, sensor fusion, data processing, visualization, and system integration expertise.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	1400	1900	900	300	4500
NAVY	2800	4300	1500	0	0	8600
NASA/JPL	2000	2400	2600	0	0	7000
TOTAL	4800	8100	6000	900	300	20100

12. Performers:

CSS and JPL are the lead performers. The magnetic sensors for MUDSS will be supplied by International Business Machines and/or Quantum Design; the sonars will be supplied by Westinghouse; additional major contractors will supply the EO sensor and system integration support.

13. Principal Investigator:

John D. Lathrop
Code 10T2, Coastal Systems Station
NSWC, Panama City Detachment
Panama City, FL 32407-7001
Phone: (904) 234-4667
Fax: (904) 235-5462

14. Keywords:

gradiometry, acoustics, electro-optics, mass spectrometry, fusion

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup
2. **Project Title:** Rapid Detection of Explosives and Other Pollutants
3. **Agency:** Navy
4. **Laboratory:** Naval Research Laboratory
5. **Proposal ID:** #028
6. **Problem Statement:**

This 6.2/6.3 proposal addresses Requirement 1.III.1.i. "Improved sensor technologies for measurement of environmental pollutants." The DoD has over 1200 sites contaminated with explosives and 87% of these exhibit contamination in the groundwater. Remediation of munition sites contaminated with explosives and monitoring of the surrounding area requires accurate analyses of field samples. Tests should be conducted rapidly and on site for the most effective remediation to proceed. Recent advances in antibody technology have allowed the introduction of immunoassay techniques to environmental monitoring. Unlike the sophisticated detection systems used in laboratory analysis, including atomic absorption spectrometers or gas chromatographs, immunoassays are specific for each target molecule. Existing immunoassay methods are also sensitive enough to detect molecules at the ppm and ppb level. Immunoassays now being marketed for environmental analysis, such as products from Ensys and Editek, while extremely selective, have several disadvantages for field use. First, the tests require multiple, timed steps, or user manipulation. Also, these techniques measure single samples rather than flow streams. Finally, costly reagents are used for each test, whether positive or negative.

NRL has developed a biosensor which can be configured to measure either discrete samples containing explosives in under one minute or to monitor process streams at timed intervals. Using a displacement immunoassay, multiple samples can be injected into a microcolumn containing a fluorescent explosive molecule bound to immobilized antibody. If explosives are present in a sample, the fluorescent molecule is displaced and detected. If the sample contains no explosive molecules, reagents are not expended.

The objective of the present work will be to use the existing biosensor for TNT and DNT to test soil and water samples from known sites of contamination. Operating parameters for selected molecules, including detection limits, possible interferents in samples, and useful system lifetime will be investigated. If the laboratory studies are successful, we will perform on site analyses for explosives.

This effort will be a demonstration of technology already developed at NRL to detect explosives. The proposed work will be a new project for the SERDP . Previous work on the explosive biosensor was performed under the sponsorship of the Federal Aviation Administration Technical Center.

7. Project Description:

An assay for the explosive trinitrotoluene (TNT) using the flow immunosensor and fluoresceinated TNT as the signal molecule is already well-developed and thoroughly tested on aqueous laboratory samples. An assay for the plastic explosive PETN is also being optimized. To adapt this technology for site characterization, the primary tasks in the first year of funding will be to look at field samples on the laboratory device and minimize problems due to background noise from interferents. Since environmental samples often contain multiple species which could interfere with fluorescence detection, particularly at emission wavelengths less than 550 nm, it is necessary to examine field samples for intrinsic fluorescence and select a signal molecule that fluoresces outside the range of background noise. Fluorescein, the principal label used to date for the signal molecule, emits at 520 nm--a region for which some background signal would be expected. Several new fluorescent dyes have become available recently that have the potential to greatly reduce the problems. Two of these dyes, Cy5 and Cy3, are excited in the red region (630-650 nm excitation), where there is little natural fluorescence from the environment. There are also good, low cost diode lasers which can be used for the flow sensor instrument at these wavelengths. These dyes, as well as others that emit in the upper wavelenths, will be linked to TNT and tested as signal molecules in the flow immunosensor. Samples of TNT will be spiked into buffer and into environmental samples to confirm the sensitivity of the assay.

Field tests will be conducted on soil and groundwater samples using our current lab prototype at the selected test site. For confirmation of results, an independent test for the presence of the compounds in the sample will be done. This will involve performing a separate analysis such as gas chromatography/mass spectrometry (GC/MS) on the sample.

If the proof-of-principle tests for environmental monitoring with the flow immunosensor are successful, work will proceed on engineering a portable device. The flow immunosensor developed at NRL is currently a laboratory prototype. Though transportable enough for field tests, the system still requires two heavy carrying cases, and is dependent upon an outside source of electricity. We have discussed the possibility of constructing a shoebox-size device with several small businesses, including Universal Sensors, Micro Fluid Systems and Physical Optics Corporation. Each claims that there should be no problem engineering an effective, user friendly, and inexpensive device.

8. Expected Payoff:

The flow immunosensor has many advantages over existing technologies. Operation of the sensor is straightforward and fast, and does not require a skilled operator or extensive training. The prototype now in use requires only two computer keystrokes. In its simplest version, the user introduces the sample at the beginning of the system and records the results within 1 minute of sample introduction. Again, this is in contrast to the user intensive and time consuming operation of currently available detection devices. The widely used methods often require addition of different reagents throughout the assay and lengthy incubation times, or demand the use of large, sophisticated instruments. Even if an initial sample extraction procedure is required, the solvents required are less noxious than the solvents used to prepare samples for GC or HPLC analysis. In the NRL sensor, all the components required to recognize the target in an aqueous solution and release a signal are contained within a small column.

The flow immunosensor is also well-characterized. Experimental parameters, including column size, antibody density, and flow rate, have been studied extensively. Using a mathematical framework recently developed, we are able to predict the behavior of the sensor for a given antibody-analyte pair. In addition, because the immunosensor is antibody-based, detection is extremely specific for the target molecule.

System manufacturing costs and portability are also important considerations. The components of the current system are inexpensive and off-the-shelf. Cost for the laboratory prototype is under $10,000, and the sensor can be engineered to fit into a single briefcase with microprocessor control.

An additional strength of the NRL flow immunosensor is its adaptability for use in a variety of environments. It can be readily used with individual samples injected by hand, air samplers that extract vapors into water, or super sipper systems that rapidly inject samples from hundreds of vials. If initial field tests results are positive, the instrument could be easily reconfigured to allow for monitoring contaminants in process or waste streams. Alternatively, it could be configured to analyze samples individually introduced as the device is moved from place to place. If the samples are not in aqueous medium, they will need to be prepared by the extraction procedures developed specifically for the explosives.

Finally, the detection limit of the flow immunosensor is already comparable to established, more complicated systems. Using the NRL sensor, TNT in water has been detected at levels below 5 parts per billion (equivalent to 5 ng/ml). This level of sensitivity is well beyond that obtained using precipitation, dip stick, most enzyme immunoassays, and fluorescence polarization methods, and is comparable to radioimmunoassays.

The flow immunosensor has already been shown to have extreme specificity, sensitivity, and the versatility required to detect a wide range of molecules. This technology will be particularly relevant for testing groundwater, streams and lakes for wastes from explosive manufacture, for monitoring chemical & fuel storage, and for checking the progress of bioremediation-compliance efforts. If married to air samplers and aqueous extracts of soil samples, the device can also be used for monitoring ground contamination.

9. Milestones:

1.	Adapt sensor for TNT detection in field samples	2/94
2.	Determine limits of sensitivity and column lifetime for analysis of samples	3/94
3.	Conduct tests on environmental samples in the lab and in the field	9/94
4.	Build portable device	6/95
5.	Lab test portable device	9/95
6.	Field test portable device	9/96

10. Transition Plan:

This technology has already been successfully transferred to private industry on an exclusive license for drug detection applications only. Development work for this effort was conducted under a CRADA. In addition, the USDA is actively pursuing the development of a flow

immunosensor for pesticide detection. Finally, the EPA has requested that NRL work with them to develop a device for PCB and PAH detection and process control.

11. Funding: ($K)

	FY94	FY94	FY95	Total
SERDP	100	200	200	500

12. Performers:

The primary performers for this project will be personnel from NRL's Center for Bio/Molecular Science and Engineering. The portable device will be fabricated by a small business.

13. Principal Investigator:

Anne W. Kusterbeck
Code 6900
Naval Research Laboratory
Washington, D.C. 20375-5348
Phone: (202) 767-4303
FAX: (202) 767-1295

14. Keywords:

Biosensor, immunoassay, environmental monitoring, antibody/antigen, fluorescence detection

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Toxicology and Human Health Risks

3. **Agency:** U.S. Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Proposal ID:** #115

6. Problem Statement:

Chemical contamination of groundwater and soil is a national problem which consumes extensive technological and financial resources. Cleanup levels are determined on the basis of risk calculations, usually requiring extrapolation from laboratory animal studies. Determining acceptable levels for humans from animal studies is a conservative, policy driven process that involves extrapolation and interpretation of scientific findings. Scientific uncertainties in this process are often compensated for by conservative assumptions that result in lower cleanup levels with inherent increased costs.

Current costs to clean up to the low ppb range in water and soil are in the hundred of millions of dollars. Operating costs of a groundwater treatment system for a single plume at Wright-Patterson AFB, contaminated with high levels of trichloroethylene (TCE), are $1.3 million/year. TCE remediation at 31 DoD installations has cost $670 million to date, while work for all solvents has cost $2 billion. It has been estimated that for 125 Air Force sites with TCE contamination, raising the drinking water standard from 5 to 50 ppb would save $620 million.

TCE, tetrachloroethylene, and other volatile organics are priority groundwater contaminants for DoD and the US EPA. These chemicals often greatly exceed current risk-based cleanup levels at Superfund landfill sites. This project is designed to further the development of newer risk assessment methodologies for developing reasonable health protective criteria for important groundwater contaminants for use in establishing cleanup requirements.

7. Project Description:

The goal of this project is to develop innovative risk assessment methods that are applicable to common volatile organic water and air contaminants for use in development of scientifically defensible cleanup criteria. Objectives have been defined in each of the areas of the four step risk assessment process: hazard identification, exposure assessment, dose-response assessment, and risk characterization. The objectives focus particularly on the critical dose-response assessment step in light of the efforts by US EPA to adopt revised guidelines for Cancer Risk Assessment. TCE will be used as the case study chemical for development of these approaches concluding with development of Provisional Remediation Goals.

This project is a joint venture for Air Force, Army, Navy, and US EPA that has had national and international input and cooperation from academic and industrial sectors. Many elements of this program were reviewed and supported at an international TCE Workshop which included nearly 40 leading researchers and policy analysts from academia, industry, US EPA, and DoD in areas

of epidemiology, metabolism, pharmacokinetic modeling, tumor promotion, peroxisomal proliferation, biological effects modeling, and risk assessment.

This project is an enhancement of a previously funded SERDP applied (6.2) project. It contributes directly to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: 1.V Risk/Hazard Assessment and 1.X: Hazard Assessment. Methods developed in this project are generally applicable to the development of risk based criteria.

Objective 1: Evaluate new EXPOSURE ASSESSMENT approaches to address the future use scenarios used to derive cleanup criteria.

1.1 Evaluate utilization of probability (Monte Carlo) analysis for future use exposure scenarios for volatile organics in water such as drinking (oral) or showering (inhalation).

Objective 2: Improve DOSE estimation across species (mouse, rat, human) using physiologically based pharmacokinetic modeling and supporting research.

2.1 Expand PBPK modeling beyond its current strength with volatile organics, to better address toxicologically relevant water soluble compounds such as metabolites of TCE.

2.2 Improve quantitative descriptions of the metabolic pathways and uptake mechanisms for TCE and its metabolites in mice, rats, and humans using appropriate *in vivo* and *in vitro* laboratory studies.

2.3 Evaluate the pharmacokinetic competency of carcinogenic metabolites of TCE to account for the cancer induced by the parent compound.

Objective 3: Improve RESPONSE comparisons across species using alternative modeling approaches and supporting research.

3.1 Evaluate the correlation of biomarkers of the cancer process with production of radicals during TCE metabolism.

3.2 Develop conceptual frameworks for biological based dose-response (BBDR) modeling to integrate pharmacokinetics (exposure, dose, tissue-dose) with markers of early and late biological responses.

Objective 4: Propose new RISK CHARACTERIZATION strategies for utilization in development of cleanup criteria.

4.1 Evaluate the implications of alternate dose-response modeling methods for acceptable risk levels.

4.2 Recommend Provisional Remediation Goals for TCE to DoD and draft suggestions to US EPA for TCE risk assessment under new EPA guidelines.

Tables 1 and 2 outline the project and indicate those elements funded by SERDP or other sources. Table 3 lists planned deliverables (according to funding year). Further details are presented in Attachment 1.

8. Expected Payoff:

One result of this effort will be to persuade the US EPA to revisit the cancer potency calculations for TCE under the new proposed guidelines for cancer. Within the next year or so, dioxin will go through this process. Central to the dioxin issues is the use of a biologically-based response model. Our goal is to have TCE be the second chemical that goes through the new cancer guideline evaluation process. The result could be savings of millions of dollars.

Two critical elements are required in working with US EPA. One is to build up the supporting peer reviewed scientific literature to support their decision making. The other is to provide alternatives to the default methodologies that they normally employ. These methods generally incorporate greater scientific information to minimize the use of conservative default assumptions.

This project is designed to provide both of these elements. Alternative risk assessment methods will have great applicability to other volatile organic chemicals whether for developing cleanup criteria, evaluating pollution prevention alternatives, or establishing operating limits on environmental emissions.

9. Milestones:

1.	EPA funded research (initiate)	11/93
2.	PBPK model development for metabolites (initiate)	11/93
3.	Biological effects research (initiate)	11/93
4.	Define field exposure paradigm (initiate)	12/93
5.	Develop comprehensive research proposal for TCE	12/93
6.	TCE Science Workshop meets	12/93
7.	Development of analytical methods (complete)	9/94
8.	Decide if pathogenesis study will be implemented	12/94
9.	DCA metabolism research (complete)	12/94
10.	Probability analysis of exposures in water (complete)	3/95
11.	Low dose extrapolation for tumor promoters (complete)	6/95
12.	Cross species comparisons: TCE metabolism (complete)	9/95
13.	Comparative dose route bioeffects studies (complete)	12/95
14.	Validation of PBPK model (initiate)	1/96
15.	Linking PBPK models for metabolites and TCE (initiate)	1/96
16.	Prepare draft position paper on acceptable risk	6/96
17.	Interspecies pharmacokinetics (PBPK models) (complete)	12/96
18.	Complete TCE pathogenesis study	6/97
19.	Provisional Remediation Goal for TCE (complete)	12/97
20.	Comments to EPA on TCE cancer risk assessment (complete)	12/97

Milestones for key deliverables are underlined.

b. Milestone Analysis

	Accomplishments -	SERDP 92
JUN 1993	APR 1993	Install GC/LC-MS for Metabolism Studies
OCT 1993	DEC 1993	Install, Validate Human Liver Slice System
MAR 1993	(ongoing)	Human Metabolic Studies for TCE

OCT 1993	JAN 1994	Complete Metabolic Interaction of TCE/VC for Risk Assessment
JUN 1993	FEB 1993	Dosimetry TCE Risk Assessment
OCT 1993	(on hold)	Refined Dosimetry TCE Risk Assessment (on hold per TCE Science Workshop)

Accomplishments to Date - SERDP 93

NOV 1993	JAN 1994	Fund US EPA
DEC 1993	DEC 1993	TCE Research Proposal
DEC 1993	DEC 1993	TCE Science Workshop

10. Transition Plan:

The first step was to have an expert group (TCE workshop), which includes the US EPA, endorse the research issues that need to be addressed in order for the US EPA to revisit the US EPA's TCE potency calculation for cancer. This involved industry, government and academia. AFOSR (6.1) monies are being used to leverage the research costs in house. American Waterworks Association is funding a few university grants and Dow Chemical is conducting environmental fate and neurotoxicity studies. The Air Force is leading the effort to bring together the regulatory and research scientists to address this pressing national environmental problem.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	1700	1400	1400	1400	5900
EPA	700	700	700	700	2800
USAF	200	300	300	300	1100
ARMY	200	200	200	200	800
NAVY	150	120	120	120	510
Total	2950	2720	2720	2720	11110

AGENCY	TASK	COST	DELIVERABLES
USAF	1. Comparative in vitro metabolism studies: TCE and metabolites in mouse, rat, human	200K	Peer Review Publication (PRP)
	2. Pharmacokinetic studies in mouse for TCE	100K	PRP
	2. Biological markers for TCE carcinogenicity (free radicals, lipid peroxidation)	215K	PRP
	3. Benchmark dose for tumor promotion	100K	Position paper
	5. Admin (5%)	85K	PRP
US EPA	1. Extrahepatic metabolism	150K	PRP
	2. Extrahepatic response assessment	150K	PRP
ARMY	1. Exposure pathway analysis	200K	PRP

NAVY	1. PBPK modeling and studies for water soluble metabolites of TCE	200K	PRP

12. Performers:

This research is being conducted by the US EPA/OHEA, Army (SGRD-UBG-O), Navy (NMRI/TD), and USAF (OL AL HSC/OET). Dow Chemical Company in Midland, Michigan; Colorado State University; Washington State University; Medical College of Toledo and the University of Georgia are involved in related research activities.

13. Principal Investigator:

Jeffrey W. Fisher, Ph.D.
OL AL HSC/OET Bldg 79
2856 G Street
Wright-Patterson AFB, OH 45433-7400
Tel: (513) 255-3423
Fax: (513) 255-1474

14. Keywords:

Risk Assessment, Trichloroethylene, Cleanup, Cancer, Dosimetry

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Cleanup

2. Title: Hazard Assessment Techniques & Biomonitoring Technology

3. Agency: Army

4. Laboratory: US Army Biomedical Research and Development Laboratory

5. Proposal ID: #717

6. Problem Statement:

The assessment of potential hazards to human health and ecological receptors posed by complex environmental contamination drives the cleanup and compliance decisions made by Federal risk managers. From site prioritization to remediation efficacy demonstration to long term monitoring required by Federal law, the question of how we decide what is "clean" is the central determinant in decisions affecting the annual expenditure of billions of dollars. Analytical chemistry data and subsequent single chemical risk assessment calculations involving numerous conservative assumptions have been the principal tools, to date, for program managers accomplishing their remediation missions. The opportunity to more realistically define these hazards, however, would optimize the expenditure of limited remediation resources and enhance the confidence risk managers and the public have regarding the efficacy of cleanup activities. The use of biological models to integrate exposure to complex chemical mixtures in the environment and then determine the actual hazard that the contamination may pose has long been a subject of in-house research in a number of agencies. Researchers have often been handicapped, however, by their inability to gain access to contaminated sites on which research applications may be further validated and new concepts pursued to insure the best possible tools are developed for remediation managers.

7. Project Description:

The Research Methods Branch (RMB) of the US Army Biomedical Research and Development Laboratory (USABRDL) has developed a biological assessment approach to assessing the hazards posed by chemical contamination of the environment. This research has been supported principally with Army Corps of Engineers funding in DA Projects BS04 and 835. Defense Environmental Restoration Program R&D funds were used by RMB scientists to develop 2 mobile biomonitoring research facilities each consisting of 3 mobile labs. These platforms enable scientists to conduct sophisticated on-site research concerning the biological effects of exposure to complex environmental contamination in aquatic, terrestrial, and atmospheric media. Research has been initiated based from these facilities at Aberdeen Proving Ground (APG), MD and will be started in FY94 at Rocky Mountain Arsenal (RMA), CO. Interest in the RMB research has also resulted in a planned technology demonstration of the mobile biomonitoring facility at a Department of Energy (DOE) site early in FY95. These sites present unrivaled research opportunities given the scope and complexity of their chemical contamination and remediation missions, the variety of ecological and human health concerns present, and the potential for the development of tools applicable to other Federal sites. These RMB research platforms operated at Federal sites will provide the nucleus of the proposed research initiative.

Personnel from Research Methods Branch, GEO-CENTERS, Inc. (the RMB in-house contractor), Experimental Pathology Laboratory (under contract to RMB), and Engineering Computer Optecnomics (partners with RMB pursuant to an IAG with DOE) will establish and man the mobile biomonitoring research facilities. The locations for the on-site research projects will consist of staging and support areas at Fort Detrick, MD for Mid-Atlantic activities or Colorado State University (CSU), CO for Intermountain activities as well as the aforementioned Federal facilities for the specific research projects. Agreements in principal have been obtained from CSU, APG, RMA, and DOE for the siting of the biomonitoring facilities and conduct of the proposed interagency biomonitoring research project. RMB research activities will consist of the validation of techniques used in an Integrated Biological Assessment approach developed at the fixed lab facility at Fort Detrick. This will include the validation of the USABRDL-sponsored Frog Embryo Teratogenicity Assay-Xenopus (FETAX) in an on-site mode. The protocol for the conduct of FETAX has received American Society for Testing and Materials (ASTM) approval and an Atlas of Abnormalities has been published. The proposed project will extend the use of FETAX to on-site applications and eventual transition to use by remediation program managers. Chronic toxicity assays will be employed including sophisticated histopathological assessments of animals exposed to multiple concentrations of on-site mixtures. Endpoints include organ-specific toxicity, carcinogenicity, immunotoxicity and reproductive toxicity. Analytical chemistry and mutagenicity assays will also be conducted. Meta-analytical statistical approaches will be employed to provide new decision oriented tools for risk managers.

US Geological Survey (USGS) scientists will use the RMB Analytical Chemistry module of the mobile Biomonitoring facility to study the exposure pathways of chemical contamination. In the proposed study, a plume of volatile organic contaminants will be tracked along a major ground-water flowpath through the wetland, extending from outside the wetland area to the endpoint in a creekbed at APG. The primary purpose of this study is to define the hydrological and biogeochemical processes controlling the fate of trichloroethylene along this flowpath. Most chlorinated volatile organic compounds, including trichloroethylene, are more easily degraded by microorganisms in an anaerobic environment than in an aerobic environment. Thus, the marsh area may be important in enhancing the biodegradation of contaminants. Biodegradation can produce intermediate compounds that are more mobile and toxic than the parent compounds. For example, biodegradation of trichloroethylene under anaerobic conditions can produce vinyl chloride, which is more toxic than trichloroethylene. However, if complete biodegradation of the compounds ultimately occurs, nontoxic compounds of carbon dioxide and water are the final products. A combination of field and laboratory studies will be used to define the hydrologic and biogeochemical processes controlling the fate of trichloroethylene. These studies will also provide specific sample collection points for selected biomonitoring techniques.

Scientists assigned to the Walter Reed Army Institute of Research and the US Air Force's Armstrong Laboratory at Wright Patterson AFB (WPAFB) will develop a multi-compartment physiologically based pharmacokinetic (PBPK) model to describe tissue disposition of the component chemicals of a complex mixture. Rats will be exposed to a mixture of trichlorethylene (TCE), vinyl chloride, and tetrachloroethane for two weeks. Metabolites will be identified and kinetic data obtained for the components of the mixture. A PBPK model will be developed, initially focusing on the blood and liver compartments, and a pharmacodynamic description of enzyme induction will be incorporated as data are developed. Such a biologically based model will integrate mechanistic pharmacokinetic data by identifying the determinants of chemical deposition within the body and model compartments. This work will build on the expertise available at WPAFB in the field of modeling, and will used data obtained in previous

exposure of animals to single chemical constituents of the complex mixture. After a laboratory study with rats is completed lab work and field studies with an aquatic species will be performed by RMB in biomonitoring facilities. Data will be used to develop a PBPK model for the aquatic species, and a comparison to rat and human PBPK models will be made. These data will aid in determining dose extrapolations to be used in complex mixture hazard assessment calculations.

US Environmental Protection Agency (EPA) scientists will extend mobile on-site testing to estuarine organisms. A toxicity test using embryos of the grass shrimp Palaemonetes pugio will be adapted for use in the RMB mobile lab and applied to suspected pollution at coastal sites at APG. The sensitivity of the shrimp embryo test for environmentally important hazardous chemicals will be evaluated in the laboratory at the EPA Environmental Research Lab at Gulf Breeze, FL. These tests will then be adapted for use in the mobile unit and validated at APG. The medaka (Oryzias latipes) is the principal fish species used as a model for carcinogen studies by the Army. Current carcinogen testing with medaka is performed in freshwater conditions even though these fish can withstand relatively high salinities. Laboratory studies will be undertaken to expose medaka in saltwater conditions to at least three environmentally relevant carcinogens and lesion formation will be compared histologically with identical exposures in fresh water. Results will identify differences in sensitivity, potential complications and usefulness of medaka carcinogenicity studies to a mobile unit assigned to coastal bioremediation sites. Studies involving the development of biomarkers for carcinogenesis using apolipoprotein A-1 and vitellogenin will also be conducted. Animals exposed in the RMB biomonitoring facility will also be examined in an attempt to isolate and identify unique proteins and/or nucleic acid alterations which may be useful as predictive biomarkers to assist in the interpretation of chronic bioassay results. Antibodies to these biomarkers will be developed to allow the subsequent examination of similar lesions in feral populations of animals inhabiting areas adjacent to the contaminated sites.

US Fish and Wildlife Service (USFWS) scientists will develop and use a suite of assays to facilitate the assessment of terrestrial and aquatic contamination. This research will include the Sediment Quality Triad to integrate laboratory toxicity data, chemical analyses and benthic community assessments. Specifically, the toxicity of whole-sediment and pore water will be assessed with the amphipod Hyalella azetca or other appropriate benthic organisms. Pore waters and sediment elutriates will be obtained on-site in RMB biomonitoring facilities or from sediments brought into the laboratory. USFWS scientists will also standardize behavioral and physiological measures of neurotoxicity to assess contamination. This will complement routine assessment procedures currently in use by DoD including the FETAX assay and acute toxicity assays. Methods for measuring contaminant impacts on the neurotransmitters, serotonin and acetylcholine, which are associated with a number of physiological and behavioral functions will be developed. The heme synthetic pathway is sensitive to both organic and inorganic pollutants. The status of the heme synthetic pathway in fishes from selected sites for evidence of chemical exposure will be investigated. New technologies in biochemically-based bioanalytical assays for the evaluation of complex mixtures of environmental contaminants show promise as tools to address the need for rapid, cost efficient, methods for analysis of samples. Immunochemical assays which utilize monoclonal antibodies for specific target analytes will be developed and validated for environmental contaminant analysis. The immunochemical components of this work will focus on the development and validation of new and existing antibodies toward specific environmental contaminants. Toxicity Identification and Evaluation (TIE) procedures will be applied to assist in identification of environmental contaminants. The Semipermeable Membrane Device (SPMD), an efficient means of determining the level of biologically available

contaminants in water and sediments (i.e. pore water) will be used to ascertain the presence of lipophilic contaminants for biochemical assays (eg. EROD, AHH, etc.). Heavy metal concentrations in aquatic ecosystems are also a major problem in environmental health. However, major gaps exist in current methodology for determination of heavy metal residues. Methods will be developed using the SPMD approach for sequestering heavy metals. This will involve modifications involving the membrane components as well as the sequestration media. Methods will be developed for ionic species and organometals (often the most toxic species). The relative abundance of sensitive macroinvertebrate taxa has long been recognized as an effective indicator of contaminant exposure. However, most of the methods and metrics used in benthic ecological investigation have been devised for use in open water; they are poorly defined for wetlands. The results of both active (grab samplers and dredges) and passive (artificial substrates developed by NFCRC) sampling methods to characterize wetland benthic communities exposed to DoD-derived contaminants will be developed and evaluated.

University-based scientists will also participate in the proposed research on the development of improved biomonitoring techniques. Preproposals are being received from scientists to use the RMB facilities for the conduct of biomonitoring and hazard assessment research. These projects will include the use of honeybees to assess complex contaminant mixtures containing military unique chemicals. Honey bees are efficient multi-media monitors of contaminant exposures and biotic effects. The goal is to provide affordable American Society for Testing and Materials ASTM certified methods using bees to discover and manage these chemicals. The model can be used to design ecological assessments and to evaluate whether observed responses are due to natural variability or anthropogenic factors, such as exposure to a toxic chemical. Other investigators will conduct research evaluating the effects of heavy metal contamination on benthic communities for use in an ecological impact assessment. An Index of Community Sensitivity (ICS) approach will be developed using individual species sensitivity measures and the relative abundance of dominant taxa at a given site. These scientists will also explore the development of inexpensive biomarkers of exposure and effect using the planaria. Phylogenetically conserved targets will be used for the development of cancer and reproductive toxicity biomarkers.

The USEPA proposal entitled "Use of Molecular Toxicology to Assess Site Hazard" and the Army Waterways Experiment Station proposal entitled "Rapid On-Site Chemical/Toxicological Analysis" will use the deployed RMB Biomonitoring Facility for portions of their proposed research, as well.

8. Expected Payoff:

The deployment and use of the Army-developed Mobile Biomonitoring Research Facility (MBRF) will afford a unique opportunity for research scientists from Federal, private and academic sectors to work collaboratively on the development of enhanced hazard assessment techniques & biomonitoring technology thus leveraging existing efforts in this area. The innovative methods selected for research in this project are those that show the greatest potential for use in monitoring, assessment and characterization activities in several agencies of the Federal government. The knowledge gained by this effort will significantly enhance our understanding of the possible impacts of complex chemical contamination of the environment. The specific methods developed when transitioned to the remediation or compliance communities will focus efforts on those sites posing the greatest threat to human health and/or the ecology insuring the most efficient expenditure of limited resources. These methods will also significantly improve

monitoring capabilities at contaminated sites thus enhancing public confidence in critical environmental programs.

9. Milestones:

1. Establish MBRF at APG	01/94
2. Conduct lab based assay development in respective lab	04/94
3. USFWS projects begins at APG MBRF	04/94
4. Initiate FETAX and USGS project at APG	05/94
5. Delivery of second MBRF	06/94
6. Establish CSU base lab	07/94
7. University research initiated at APG MBRF	08/94
8. WES biomarker project at APG MBRF	08/94
9. EPA studies begin at APG MBRF	11/94
10. Annual review meeting	03/95
11. DOE biomonitoring demonstration project	04/95
12. Second MBRF site selected (ie. RMA)	04/95
13. WES biomarker project at APG MBRF	11/95
14. Annual report published	11/95
15. EPA Molecular Tox projects begin in MBRF	11/95
16. Annual review meeting	04/96
17. Annual report published	09/96
18. Initial methods transfer to user (ie. APG, RMA)	09/96
19. Annual review meeting	04/97
20. Annual report published	09/97
21. Full Integrated Assessment package provided to user community	06/98
22. Final review meeting	06/98
23. Final report published	09/98

10. Transition Plan:

In addition to the publication of scientific papers in peer-reviewed journals and Agency-specific Technical Reports, an annual meeting of all scientific participants will be held and a proceedings published. Representatives from Installation Restoration staffs of DoD and DOE will also be invited to attend this meeting. Coordination and technology transfer to EPA will be accomplished through Dr. William Farland, Director, Office of Health and Environmental Assessment, Office of Research and Development. Coordination and technology transfer with the Department of Interior will be accomplished through Mr. Wilbur Mauck, Assistant Director, National Fisheries Contaminant Research Center. APG specific reports and methods will be coordinated through Mr. Ken Stachiw, Chief Environmental Conservation & Restoration Division, APG. RMA specific reports and methods will be coordinated through Mr. Brian Anderson, Chief, Remedial Planning Branch, Environmental Engineering Division, RMA, CO. New methods developed, validated, and selected for use will be provided complete with Standard Operating Procedures and sample Scopes of Work to remediation program managers with specific instructions regarding use of the methods and interpretation of data. Reports of interest to remediation managers will be forwarded following scientific and policy review by the respective Principal Investigator's Agency.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	1745	2080	2145	1790	875	8635

12. Performers:

This multi-Agency proposal will involve RMB personnel and the RMB-developed mobile labs as well as scientific experts from a number of Federal, Academic and private institutions. The research effort will be led by Points of Contact (POC) from each performer with the lead responsibility for management and coordination provided by the US Army Biomedical R&D Lab, Research Methods Branch. POC's from each performer are as follows:

USABRDL, RMB: POC Mr. Hank Gardner, Dr. Bob Finch; Walter Reed Army Institute of Research , US Army Medical Research Detachment: POC LTC Dan Caldwell;
US Air Force Armstrong Laboratory, Occupational and Environmental Health Directorate, WPAFB: POC Dr. Jeff Fisher; USEPA Environmental Research Lab, Gulf Breeze: POC Dr. William Fisher, Dr. Jack Fournie, Dr. Leroy Folmer; US DOE Morgantown Energy Technology Center, Environmental and Waste Management Division: POC Dr. Jagdish Malhotra; US Geological Survey, Water Resources Division: POC Ms. Michelle Lorah; US Fish and Wildlife Service, National Fisheries Contaminant Research Center: POC Mr. Wilbur Mauck, Dr. Jim Petty;
GEO-CENTERS Inc.: POC Mr. Dave Lovelady, Dr. Lorraine Twerdok; Experimental Pathology Laboratory: POC Dr. Marilyn Wolfe; Engineering Computer Optecnomics: POC Dr. Stanley Finger; Colorado State University: POC Dr. Ray Yang, Dr. Wil Clemens; University of Montana: POC Dr. Jerry Bromenshenk; University of Maryland: POC Dr. Dennis Burton.

13. Principal Investigator:

Hank Gardner
Chief, Research Methods Branch
US Army Biomedical Research and Development Lab
Fort Detrick, MD 21702-5010
Phone: 301-619-2027
Fax: 301-619-2569

14. Keywords:

Biomonitoring, bioassay, biomarker, ecotoxicology, toxicology, assessment

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Biosorption Treatment of Plasticizers and Solvents.

3. **Agency:** US Army

4. **Laboratory:** USAE Waterways Experiment Station (WES)

5. **Proposal ID:** #711

6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with low levels of plasticizers (acetone) and chlorinated solvents (trichloroethylene [TCE]). Current or traditional treatment technologies available for use in TCE treatment are granular activated carbon (GAC) and air stripping; however, neither technology results in the direct destruction of the organic contaminant. An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the near future for chlorinated solvent oxidation. Remediation costs for all of these technologies generally falls within the $1.00 to $5.00 per 1,000 gallons range. In the case of GAC, treatment of groundwaters containing low levels of chlorinated solvents is not economically feasible.

Acetone poses a very unique challenge to both traditional and innovative technologies. Acetone does not adsorb onto GAC due to its high water solubility, it does not strip in air strippers due to its low Henry's Law constant, and it does not oxidize in chemical oxidation systems due to its stable chemical structure. Acetone is degraded biologically, but biotreatment is unsuitable for treatment of low level contaminated groundwaters because an active biomass cannot be sustained due to low substrate loadings. Unfortunately, most groundwaters contain acetone at relatively low levels; therefore, expensive cometabolite addition is almost always required.

TCE can also be treated using biological degradation. TCE is somewhat more difficult to biodegrade then acetone, but recent advances in cometabolic pathways (methanotrophic) indicate that biotreatment of TCE is feasible. One problem associated with TCE degradation is the tapering off of microbial activity, over time, in continuous and semi-continuous biological systems. Biosorption is almost always associated with GAC. Primarily, GAC is used as a means of extending the service life of a GAC bed by regeneration of the spent carbon within the bed. Recent work on phenolic compounds has resulted in the development of an innovative technology known as biofilters. This technology utilizes GAC as a means of structurally supporting an active biomass.

Organophilic clays (OPCs), have been successfully used to remove low levels of wood preserving waste from contaminated groundwater. Results of this evaluation are encouraging, but disposal of the spent OPC is a problem. OPCs are innovative adsorbents that have received limited evaluation and application for the removal of low levels of acetone and TCE.

The USAE Waterways Experiment Station (WES) has conceptualized a treatment system for low level contaminated groundwaters based on biosorption and bioslurry systems. In this treatment scheme, the contaminants are adsorbed onto the OPC until all adsorption sites of the OPC are

spent. The spent OPCs are removed from the reactors, ground into small particles, and then an on-site bioslurry reactor is used to biologically degrade the adsorbed contaminants. This converts OPC adsorption from a simple phase-change technology into an on-site destruction technology.

This proposed treatment approach is an applied research and technology field pilot application (6.2). This research is an enhancement to an existing FY 93 SERDP proposal.

Specific identified user requirements to be addressed through performance of this work unit include:

1.I.1.b. Technology for removal of energetics/other organics contamination.
1.I.1.f. Treatment system for water contaminated with organic contaminants.
1.I.1.g. Treatment system for water contaminated with chlorinated and defense hydrocarbons.
1.I.1.j. Treatment of Navy revelent contaminants in salt/brackish/groundwater matrices.
1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
1.I.1.h. Treatment system for water contaminated with mixtures of chlorinated solvents.
1.I.2.i. Contamination under buildings and roads.
1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
1.I.2.e. Improved marine sediment remediation technologies for metals, organics, and PCBs.
2.III.1.d. Enzyme and bacterial treatment technology.

7. Project Description:

The USAE Waterways Experiment Station (WES) under the Environmental Quality and Technology Program (EQT) is developing a means of biologically regenerating spent GAC. WES also plans to evaluate the use of OPCs for treatment of explosives contaminated groundwater. It is believed that OPC biosorption can be utilized for the treatment of low level explosive contaminated groundwater.

The USAF Tyndall AFB has been active in development of microbial consortia capable of effectively degrading TCE from contaminated groundwaters. This technology can be tailored to interact with the conceptualized OPC biosorption schemes. Tyndall AFB is currently developing a bioreactor for treatment of contaminated groundwater with higher levels of TCE. The consortia developed in these efforts will be useful in the development of the OPC biosorption concept. Tyndall has also developed a surfactant which may further enhance the sorptive capacity of the OPCs. An increase in sorptive capacity will result in improved costs benefits. There has been little or no direct development of OPC biosorption. Past efforts on bioregeneration of spent GAC containing phenolic compounds indicates promise for the use of microorganisms to degrade adsorbed compounds.

A recent evaluation of OPCs for wood preserving waste treatment indicates the utility of OPCs for groundwater remediation. Unfortunately, there are few options for disposal of spent OPCs (and GAC). Under US Environmental Protection Agency funding, WES has demonstrated the feasibility of using bioslurry systems for treatment of soils contaminated with plasticizers and wood preserving wastes. The contaminated soils used in these studies did contain significant clay fractions.

Tyndall AFB has demonstrated the feasibility of biologically treating TCE using aerobic microorganisms. Much of this work has resulted in the development of a microbial consortia that demonstrates excellent activity toward chlorinated solvents.

The overall objective of this study is to develop a OPC based biosorption process. Development of this technology will, in the case of acetone, provide environmental engineers with a practical means of treating acetone. With respect to TCE, this technology may eliminate the problem of TCE activity loss over time.

The development of OCP biosorption into a fieldable technology for site remediation will be approached through a series of tasks detailed below:

a. Task I. The adsorption capacity of various OPCs and other sorbents will be preliminarily evaluated by contacting the sorbent with spiked solutions containing acetone and TCE. Three to four sorbents will be selected for further testing in adsorption isotherms. Activated carbon performance will be compared to the performance of the sorbents. Cosolvency effects will be evaluated through the addition of solvents to the spiked solutions. One or two of the most effective sorbents will be selected for small column studies.

b. Task II. Evaluation of microbial activity toward adsorbed acetone and TCE. Toxicity effects of TCE concentrations on microbial consortia will be evaluated using the Microtox procedure. The ability of a microbial consortia to desorb and subsequently biodegrade the adsorbed acetone and TCE from the OPC will be evaluated using laboratory batch systems. Much of this effort will be directed toward TCE biodegradation since acetone biodegradation is much more refined.

c. Task III. Bench Scale Bioslurry Studies. Bench scale bioslurry studies will be performed to determine process feasibility, verify reaction kinetics and pathways, and set pilot studies test matrices. The bench studies will be performed using five liter all glass reactors operated in batch mode. Two oxygenase pathways, aromatic and alipatic, will be described.

d. Task IV. Pilot Scale Studies. Pilot scale studies will be performed using pilot OPC absorbers and bioslurry reactors. The complete pilot system will be designed for complete mobility to other candidate sites. If required, a process gas management system may be used if off-gassing of TCE and the selected cometabolite is deemed problematic. These pilot scale studies will be performed in the field at two DoD sites. Once completed, the pilot system will be available for field pilot application at other installations.

e. Task V. Draft Report. A report detailing the following will be drafted:

1. Describe techniques on how to perform bench scale treatability studies used for process evaluation during Feasibility Studies (FS).
2. Discuss process feasibility and potential limitations.
3. Present the results from the bench and field pilot studies.
4. Summarize available full scale equipment availability.

The report will be design and applications orientated. The report will serve as a handbook for implementation of OPC biosorption at other field sites.

The information obtained from the performance of this study will assist in meeting several DoD/DOE environmental remediation objectives. This work effort will result in the

development of a contaminant-destruction technology applicable toward both chlorinated solvent and plasticizer compounds.

Technical issues to overcome as identified to date are to determine if OPCs have appreciable adsorption capacities for acetone and TCE; if bioslurry treated OPCs can be treated to levels that render them environmentally safe and regulatory acceptable; and if process gas recirculation will be required for TCE biodegradation of the ground OPCs. This project falls under the 1.H and 1.I requirement thrust areas under the Tri-Service Environmental R&D Strategy Plan.

8. Expected Payoffs:

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. OPC biosorption treatment will fill a gap that currently exist in terms of treatment of low level acetone contaminated groundwaters. OPC biosorption may eliminate problems associated with reduce TCE bioactivity over time. The actual economic benefit is difficult to ascertain due to the innovative nature of the concept. A conservative estimate is that the technology could be implemented at a cost range of $1.00 - $3.00 per 1,000 gallons treated.

9. Milestones:

Major milestones under this work effort are listed below along with the respective fiscal year they will be completed.

Initiate the evaluation of adsorbents	3/94
Initiate microbial processes investigations	6/94
Initiate bench bioslurry systems	9/94
Complete bench scale evaluations	11/94
Design and construct pilot systems	2/95
Initiate pilot studies	4/95
Final report	10/95

10. Transition Plan:

This technology development will generally follow the typical transitional path detailed under DoD's EQT Program. Within three years, the technology will be transitioned from a bench concept to an implementable technology. Technical assistance will be available to technology users during design and implementation of OPC biosorption. Collaboration with private organizations for improving process development through CRADAs will be proposed. The technology will be transitioned to the user community through technical papers, presentations, briefings by the performers of this proposal.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	500	750	850	2100
WES	250	250	200	700
USAF	500	500	300	1300
TOTAL	1250	1500	1350	4100

12. Performers:

The performers for this work unit are USAE Waterways Experiment Station and Tyndall AFB. Advice from OPC manufacturers will be incorporated into the final technical approach for this study.

Ms. Beth Fleming
Mr. Mark Zappi
Dr. Doug Gunnison
USAE Waterways Experiment Station
ATTN: CEWES-EL
3909 Halls Ferry Road
Vicksburg, MS 39180

Ms. Catherine M. Vogel
Dr. Jim Spain
USAF Armstrong Laboratory
AL/EQW/OL
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323

13. Principal Investigator:

Ms. Cynthia L. Teeter
Environmental Engineering Division
USAE Waterways Experiment Station
ATTN: CEWES-EE-R
3909 Halls Ferry Road
Vicksburg, MS 39180
TEL: 601-634-4260; FAX: 601-634-3833

14. Keywords:

Biosorption, bioslurry, biotreatment, adsorption, trichloroethylene, acetone.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Enhancing Bioremediation Processes in Cold Regions

3. **Agency:** Army

4. **Laboratory:** Cold Regions Research and Engineering Laboratory

5. **Proposal ID:** #712

6. Problem Statement:

This project is basic, 6.1 research and has received FY93 SERDP funds. This proposal is for continued funding of the FY93 funded research and expands the scope to include rhizosphere effects. The objectives are to improve remediation ability in areas subject to low temperatures and to facilitate treating large volumes of soil at contaminated sites where low temperatures are inhibitory. Many of these sites are also subjected to extended freezing or freeze-thaw cycling, have short operating seasons, frequently have insufficient soil nutrient levels, and are often in remote locations where cost-effective alternatives do not exist. Easily implemented on-site and in-situ technologies such as biotreatment are needed for soil cleanup at these sites.

The primary strategy in bioremediation is to remove the limitations to microbial activity, but the extensive amounts of soil that are typically involved require using large-volume techniques that necessarily expose soil to seasonal temperature cycles. The net influence of freezing temperatures on the overall rate and extent of soil biotreatment is a complex interaction of microbial and chemical rates, substrate-nutrient solubility and availability, and physical-chemical phenomena. It is not sufficiently understood to exploit or manage biotreatment systems in advantageous ways.

Enhanced microbial activity in rhizosphere zones is documented for some pesticides and may offer a significant mechanism for low-cost soil treatment. Coupled with low-temperature effects, we propose to quantify low-temperature soil-rhizosphere activity and identify relationships with associated plant species. Because bioremediation is often constrained by nitrogen, phosphorus, and carbon co-substrate limitations, we hypothesize that nutrient and co-substrate limitations to bioremediation at remote sites can be overcome by stimulating soil-rhizosphere effects.

7. Project Description:

This effort applies to DoD Pillar 1-Cleanup, Thrusts 1K,1L,1M,1N, Biological Treatment of Explosives, Organics, Solvents, and Fuels in Contaminated Soils. The technical objectives are: i.) to describe, for different classes of compounds, the kinetics and endpoints of biotransformations as functions of soil moisture, available carbon, and low temperatures and ii.) to elucidate the impact of rhizospheric zones on soil bioremediation potential.

Successful application of bioremediation at low temperatures requires knowledge of how freezing induced processes influence the pathways and rates of biologically mediated processes. Recent research indicates that at lower temperatures the interacting influences of moisture, soluble carbon, and temperature on microbial activity are unpredictable from data obtained at

higher temperatures. Rate adjustments based on traditional approaches, such as scaling from laboratory studies or Q_{10} values obtained from higher temperatures, do not account for interacting phenomena encountered in field situations, and may not realistically describe processes governing bioremediation in soils exposed to severe or repeated freezing.

We have developed a system for measuring microbial activity at low temperatures and constant moisture potentials. A preliminary conceptual model is being developed from a series of laboratory experiments designed to integrate freezing and freeze-thaw influences on biological activity with chemical and physical processes. Field projects are in place to provide both authentic soil samples and field data. Freezing and freeze-thaw influences on biological, chemical, and physical processes will be integrated. Our approach will couple laboratory and field studies. Chemical structural activity relationships (SAR) will be used to select and group chemical classes of contaminants. Results will, therefore, be transferable based on structural activity relations rather than individual compounds.

Using rhizosphere effects to degrade organics is a promising, innovative technique which would be advantageous at many sites, particularly at remote locations where no feasible alternatives exist. The impact of low temperatures and extended or frequent freezing on the remediation abilities of these biological systems is unknown. Laboratory, growth chamber, and cold room studies will transition into our ongoing field projects. Plants tolerant to seasonally frozen soil and having fibrous root systems will be selected to provide improved root distribution and root-soil contact. Enhanced root exudates may provide additional carbon that is frequently needed as a co-substrate for contaminant degradation. Root mycorrhizal associations will be promoted for their positive impact on phosphorus nutrition. Legumes will be exploited for their potential for mid-depth root penetration, nitrogen fixation capabilities, and resulting microbial stimulation in poor quality soils.

In accompanying field studies, larger native plant species, acclimated to specific geographic areas and climates, will be investigated for their ability to reach deeper depths, and to recycle soil moisture and associated mobile, solution-phase contaminants through the rhizosphere and towards the soil surface, zones of enhanced microbial activity.
This research differs from previous work in cold regions bioremediation because:

a. Private industry efforts have used biopiles, treatment cells, and similar technologies. These efforts are minimally monitored with limited on-site or laboratory analysis. Documentation is sparse and restricted. Freezing effects are not addressed although treatment systems are subject to freezing.

b. EPA effort in EXXON Valdez cleanup was a coastal environment and subject to wave and storm action.

c. In-situ bioventing of lighter petroleum compounds (JP-4) in cold regions (Air Force) has focused on sub-surface, unfrozen soil systems. Improving our knowledge base may extend bioventing to environmentally acceptable use in the active zone of permafrost soils.

8. Expected Payoff:

Soil cleanup is required at military, federal, and civilian sites. Many sites are in cold, remote locations. The few alternatives that are available either use more costly, methods or incur liability due to non-compliance. Low input, scientifically defensible biotreatment alternatives

would treat such sites at minimal cost, reduce or remove liability, and minimize cleanup-associated damage to the site. The regulatory community is open to innovative biotreatment.

The results from this research are dual use and would readily transition to the public sector through field research and demonstration sites that are part of CRREL's ongoing related projects. Increased knowledge would extend the operating season and potentially provide guidance for using natural freeze-thaw cycles advantageously.

Envisioned benefits include:

a. Application to the northern tier of the continental US to extend the biotreatment operating season.

b. In-situ treatment of contamination in the active zone of permafrost soils with minimal disturbance to fragile surface ecosystems, as well as application to the northern tier of the US.

c. Transition to Arctic and Sub Arctic sites, including Northern European and Former Soviet Union sites, where conditions, location, available infrastructure, and cost preclude more intensive technologies, is highly feasible.

d. Acquired knowledge would support a dual-use technology applicable to joint DOE-DoD soil-freezing containment technology by adding a cold-adapted bioremediation capability to soils contained by cryogenic barriers.

9. Milestones:

1. Develop lab system for measuring soil microbial activity at low temperatures and constant moisture potential. 06/93
2. Based on preliminary observations, define components of conceptual model. 12/93
3. Evaluate importance of component processes, including rhizosphere effects. 06/94
4. Evaluate interactions of processes with SAR-grouped chemical classes. 06/95
5. Compare field observations to laboratory based predictions (field data collected from ongoing projects). 06/96
6. Manipulate field systems based on gained knowledge (field systems from ongoing projects) 06/97
7. Evaluate altered field systems (ongoing projects will be leveraged to serve as field experimental sites) 06/98

10. Transition Plan:

Knowledge gained from this research will transition into related 6.2 projects, Low Temperature Biotreatment, Natural Remediation, and Biotreatment of Explosives in Cold Regions. CRREL is cooperating with WES on these work units.

The high cost of conducting research at actual field sites essentially precludes using research funding alone to support field testing, but the field experimental component is fundamental to realistic bioremediation research. CRREL's strategy has been to leverage research funds by partnering with State, Federal, and private sector cooperators who are involved in cleanup operations. CRREL is currently involved in field projects through partnering programs with Alaska Science and Technology Foundation, Alaska DOT&PF (CPAR), University of Alaska

(CPAR), FAA, Air Force (Shemya and Elmendorf AFB), and private industry (Weston and Sampson Engineering, Inc., CPAR and RZA-AGRA, Inc., CPAR). These projects are primarily applied research and demonstrations; they provide authentic soil samples and field experimental sites, and facilitate laboratory-field communication. This approach also provides a real and highly visible avenue for transitioning and technology transfer, as demonstrated by our CPAR projects and cooperative projects with the Districts and Air Force. CRREL is also in the preliminary stages of developing additional cooperative field projects with private industry through CRADAs.

CRREL has coordinated transitioning with the a) Air Force, through the Engineering and Services Laboratory at Tyndall AFB and briefing the Center for Environmental Excellence at Brooks AFB on our projects. Additionally, CRREL has a cooperative project on Shemya Island through Elmendorf AFB; b) Navy, for future transitioning at the proposed Navy National Test Site and c) EPA, through the Risk Reduction Engineering Lab., Cincinnati, OH, and Environmental Research Laboratory, Gulf Breeze, FL.

11. Funding: ($K)

This research has been funded for FY93.

FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
500	700	750	800	750	700	4200

12. Performers:

CRREL is uniquely well equipped for low-temperature research and the basic research will be conducted primarily at CRREL.

This research has been coordinated with Dr. D. Gunnison at WES, the lead laboratory for cleanup. CRREL will work with Dr. Gunnison at WES to maintain coordination with related research at WES.

A limited number of Universities have recently begun research in rhizosphere-based soil bioremediation. CRREL has discussed with the EPA the potential of involving Universities and intends to do so as appropriate. We have coordinated with the Air Force, Navy, and EPA to prevent duplication and facilitate cooperation.

13. Principal Investigator:

Dr. C. M. Reynolds
US Army Corps of Engineers
Cold Regions Research and Engineering Laboratory (CRREL)
72 Lyme Road
Hanover, NH 03755-1290
TEL: 603-646-4394 FAX: 603-646-4561

14. Keywords:

Bioremediation, Sub Arctic, Freeze, Cold, SAR, Rhizosphere

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Peroxone Treatment of Contaminated Groundwaters

3. **Lead Agency:** US Army

4. **Laboratory:** US Army Engineer Waterways Experiment Station (WES)

5. **Proposal ID:** #726

6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with explosives compounds. The current or traditional treatment technology available for use in explosives contaminated groundwater remediation is granular activated carbon (GAC). An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future under the DoD's Environmental Quality and Technology (EQT) Program. Remediation costs for both of these technologies fall within the $1.00 to $5.00/1,000 gallons range. UV/chemical oxidation is advantageous to GAC because it is a destruction technology and it does not produce a waste stream (i.e. spent GAC) requiring disposal. Also, unlike GAC, UV/chemical oxidation processes are still economically viable at relatively low groundwater concentrations. UV/chemical oxidation systems are often referred to as advanced oxidation processes because they result in the formation of powerful oxidizer species such as the hydroxyl radical ($OH^\cdot$).

DoD installations requiring remediation of explosives contaminated groundwaters will require that GAC or UV based chemical oxidation systems treat literally millions to billions of gallons of groundwater. The cost to the DoD alone will be extremely high. Many environmental engineers and scientists are hopeful that *in situ* technologies will one day completely replace pump-and-treat systems that use above-ground treatment systems. Unfortunately, the technical truth of the matter is that above-ground treatment systems will always have a place in groundwater remediation activities. *In situ* treatment technologies are not a panacea. Not all sites or site situations are capable of supporting an *in situ* treatment system. More cost effective, contaminant destruction, above-ground based treatment systems are required by the DoD.

Peroxone oxidation is a groundwater treatment technology that has great potential for treating contaminated groundwaters at reduced treatment costs. The main driving force in the development and presentation of this proposal is the potential cost savings that may be incurred with the fielding of this technology. Peroxone is a chemical oxidation process that has been used primarily for treatment of drinking water in both the United States and Europe. The process involves the addition of ozone (O_3) and hydrogen peroxide (H_2O_2) into a reactor system containing the contaminated groundwater. Peroxone generates hydroxyl radicals ($OH^\cdot$) through the reaction of ozone with hydrogen peroxide. Peroxone does not require the addition of ultraviolet light to form radicals or destroy organic compounds. The hydroxyl radical is a powerful oxidizer that can destroy organic compounds into environmentally safe compounds. The stoichiometric reactions that result in the generation of the radical during peroxone treatment are listed below,

$$H_2O_2 + H_20 \rightarrow HO_2^- + H_30^+$$
$$O_3 + HO_2^- \rightarrow OH + O_2^- + O_2$$
$$O_2 + H^+ \rightarrow HO_2$$
$$O_3 + O_2^- \rightarrow O_3^- + O_2$$
$$O_3^- + H^+ \rightarrow HO_3$$
$$HO_3 \rightarrow OH^- + O_2$$

Since the process does result in the formation of radicals, it is considered an advanced oxidation process (AOP). Actual cost information obtained from French engineers indicate treatment costs as low as $0.02 to $0.10 per 1,000 gallons treated (for dilute concentrations) have been reported. This represents an order of magnitude reduction in remediation costs as compared to traditional technologies such as activated carbon and traditional UV based AOPs. Since peroxone does not require UV addition, operational problems associated with fouling of the quartz sleeves housing UV lamps or poor groundwater UV transmissivity are not of concern; thereby, eliminating a big operational concern and expense associated with UV based oxidation processes.

This work unit is proposed as a second year (6.2/6.3) project. We were approved for FY93 funding during FY93; however, to date, we have not received any FY93 funding. However, based on work performed from other funding sources on peroxone processes, the potential for using peroxone for treatment of contaminated groundwaters is even higher than originally thought. This work unit will support unfunded components of the DoD STRAT Plan and will meet or partially meet several DoD user requirements. These requirements are:

1.I.1.b. Technology for removal of energetics/other organics contamination.
1.I.1.f. Treatment system for water contaminated with organic contaminants.
1.I.1.j. Treatment of Navy revellent contaminants in salt/brackish/groundwater matrices.
1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
1.I.4.c. Decontamination of soils containing energetics materials.
1.I.2.i. Contamination under buildings and roads.
1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
1.I.4.c. Decontamination of soils containing energetic materials.

7. Project Description:

The WES has evaluated the use of peroxone processes for treatment of explosives contaminated groundwaters using bench scale peroxone reactors. Experiments using laboratory prepared solutions of TNT-distilled water have indicated that peroxone has similar removal kinetics to traditional UV based AOPs. WES, working with Mr. Randy Cerar, AEC, has evaluated peroxone for treatment of two explosives contaminated groundwaters from Milan AAP with the results being very encouraging. WES and Rocky Mountain Arsenal (RMA) have determined that peroxone has a high potential for treating groundwaters contaminated with a variety of other contaminants. Estimated costs fall within the $0.35 to $0.60/1,000 gallons treated range. WES has also performed studies using sonolytic catalyzation indicating that the addition of ultrasound may dramatically enhance oxidation reaction rate. In summary, bench efforts performed by WES indicate that peroxone processes are ready for evaluation at DoD installations using pilot scale equipment.

The overall objective of this project is to accelerate development of peroxone oxidation processes for treatment of explosives contaminated groundwaters. Process feasibility will be evaluated at both the bench and field pilot scale, with particular emphasis placed on-site pilot studies. The objectives of this project will be approached through performance of a series of research tasks. These tasks are listed and discussed below:

Task I. Determination of Reaction Pathways and Kinetics. Other funding sources will be used by WES to determine reaction pathways of explosives parent compounds. This effort will investigate oxidation pathways of environmental explosives by-products, such as amino-toluenes, which are typically found in explosives contaminated groundwaters. Since peroxone is a destruction technology, determination of the predominant oxidation pathway of selected explosives environmental by-products will be determined using laboratory solutions of buffered distilled water and reagent grade target chemicals. Only single solute solutions will be used so additional carbon sources do not interfere with pathway determination. Kinetic parameters (at minimum, peuso-first order rate constants) will also be determined. Analytical methods to be employed in determination of treatment pathways and kinetics will include high performance liquid chromatography (HPLC), stopped-flow spectrophotometry, and gas chromatography (GC).

Task II. Selection and Shipment of Groundwater Samples. Actual groundwater samples from contaminated DoD sites will be used in both the bench and pilot scale studies. This will ensure that the study remains focused on rapid field implementation. Candidate sites include Milan Ammunition Plant, Cornhusker Ammunition Plant, Sub-Base Bangor, and Hastings East Industrial Plant. Samples will be collected and shipped to WES for the bench scale studies. NOTE: All pilot studies will be performed on-site. Results from the bench testing will be used to design comprehensive pilot studies at a minimum of at least two DoD sites (one Army and one Navy). Obviously, site groundwater samples used in the bench study will be carried through to the pilot level of effort.

Task III. Bench Scale Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and oxidation pathways, estimate initial treatment cost estimates, and set pilot studies test matrices. The bench studies will be performed using one liter all glass reactors operated in semi-batch mode with respect to ozone application. Groundwater samples from various candidate pilot study sites will be evaluated in this study task. These studies will be performed at chemical oxidation laboratory of the Hazardous Waste research Center (HWRC) located at the USAE Waterways Experiment Station (WES). These studies will also investigate the feasibility of integrating ultrasonic catalyzation as a means of enhancing contaminant oxidation rate and improving mass transfer limitations. If feasible, a CRADA with a reputable ultrasound process equipment manufacturer will be initiated for collaboration in terms of adding sonolytic catalysis to the pilot system.

Task IV. Pilot Scale Studies. Pilot scale studies will be performed using a mobile pilot peroxone system with 2.5 to 15 gallon per minute operating range referred to herein as the WES Peroxone Oxidation Pilot System (POPS). Four all-glass columns plumbed in series will serve as multiple contact chambers. The system will include several automated process operations and data collection systems that will be used to fully evaluate process feasibility in the field. At least two sites containing groundwater contaminated with explosives will be treated using the pilot system. This task will verify the results derived from the bench studies, evaluate process equipment, and refine cost estimates. The WES will perform these activities with AEC and NFESC providing site management and technical support.

Task V. Draft Applications and Design Manual. A applications manual in the form of a WES report will be drafted by WES, US Army Corps of Engineers (COE)-Omaha District, and COE-Missouri River Division (MRD) for use by the user community in designing and fielding the technology. It is believed that inclusion of the design user community (COE) early in process development will ensure development of a useful and easily transferable product. Key issues to be included in the design manual are:

1. Techniques for performance of bench scale peroxone treatability studies - This information will ensure that engineering firms under contract to the installations and COE district offices will be able to properly evaluate peroxone during the FS stage of site remediation. The research team for this proposal will be available for consultation at any time during full field implementation to ensure a smooth transition of the technology from the research and development community to the user community.

2. Process feasibility and potential limitations - One important factor in development of any technology is a firm understanding of the limitations of the technology. The manual will detail all limitations and short-comings associated with implementation of peroxone that are identified. Close coordination with the full user community will be maintained during the full-field application stage to further identify any additional limitations and problems as they occur. It is believed that the manual should be a "living" document that is periodically updated to ensure that corporate memory (DoD) is not lost during implementation at various sites. Lessons learned, whether good or bad, must be recorded so that other installations attempting implementation are keep fully abreast of new technical developments in order to ensure a higher potential for successful implementation at reduced costs compared to existing technology. Particular emphasis will placed on ensuring that this information is added to various prominent technology bulletin boards.

3. Results from the bench and pilot studies - The results of both the bench and pilot studies will be presented in a concise and applications oriented manner. These results will be further transmitted to the user and regulatory communities. It is important that the regulatory community is completely confident that peroxone can be safely applied at DoD sites.

4. Summarize cost estimates and full scale equipment availability - The manual will also include full cost estimates based on the results of both the RMA and EQT/SERDP demonstrations. An assessment of available equipment will be included to assist the design engineer in equipment selection. Basically, all equipment required for peroxone implementation are already available due to its operational history within the drinking water industry and relative simplicity in terms of equipment requirements. The assessment of equipment will be oriented toward hazardous waste site remediation and the particularities associated with this unique technical and regulatory arena.

As stated above, the implementation manual will be very design and applications orientated. The manual will serve as a handbook for implementation of peroxone at other field sites. Peer review from other agencies such as the USEPA laboratories and other COE design centers will be coordinated. Potential collaboration with the USEPA's SITE Program will be pursued by WES.

Task VI. Verification of Toxicity Reduction. Toxicity assessment of both test influents and effluents will be performed to ensure significant reductions in toxicity has occurred during

peroxone treatment. Detail of the toxicology methods used will be published in the manual for use by engineering firms during evaluation of technology feasibility (i.e. FS efforts).

Key technical issues to overcome as identified to date are listed below:

a. Ensure that the parent explosives and amino based environmental byproducts are oxidized into environmentally safe, non-regulated (benign) compounds.
b. Determine if peroxone can effectively treat contamination levels typically found at DoD/Doe installations as opposed to organics levels that have traditionally associated with drinking water (which is what peroxone was originally developed for).
c. Determine the impacts of complex contamination matrices on treatment predicted from kinetic models.
d. Determining the economics and scale-up potential of ultrasound systems.

8. Expected Payoff:

The DoD has numerous sites that contain groundwaters contaminated with explosives. The existing technology, activated carbon adsorption, is costly, does not destroy the explosives, and results in the production of spent carbon which may pose a disposal problem. The WES has recently completed evaluation of traditional ultraviolet (UV) based chemical oxidation processes for treating explosives contaminated groundwaters. AEC plans to demonstrate these processes in FY94. The cost of traditional UV based oxidation processes is expected to range from $1.00 to $5.00/1,000 gallons of water treated. This is the same cost range experienced with activated carbon adsorption systems; however, chemical oxidation is much more flexible, is a destruction process, and produces no residuals requiring disposal. Peroxone processes are expected to costs in the $0.10 to $1.00 range, which represents potentially a full order of magnitude in cost savings over both activated carbon and traditional UV based chemical oxidation processes. The expected ease of system design and operational flexibility over the other chemical oxidation processes make this process appear extremely promising.

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. Peroxone treatment will economically fill a gap that currently exist in terms of treatment of low level contaminated groundwaters. Although no funding is requested for the RMA pilot studies evaluating DIMP, pesticides, and aromatics removal, performance of this work unit will improve the overall quality of the RMA study by allowing RMA/WES to use an improved pilot system then could be developed on the RMA budget alone. In return, the RMA pilot studies (FY94) will allow for evaluation of the POPS unit in terms of mechanical performance prior to performing the explosives pilot studies in FY94-96. Potential research agreements with the private section (CRADAs) will also be investigated to ensure rapid transition to the user community.

9. Milestones:

1. RMA Pilot study	5/94
2. Complete bench scale evaluations	6/94
3. Complete construction of pilot unit	6/94
4. Perform first pilot study	8/94
5. Complete first draft design package	3/95

6. Perform second pilot study 9/95
7. Final design package 6/96

10. Transition Plan:

After pilot scale evaluation of the technology is complete, transition to the user community will be accomplished through various technical reports, publications, briefings, and conference presentations. Interfacing with COE-MRD through this project partnership should accelerate transition of the technology into COE activities, while the USEPA, DOE, and USAF will be briefed periodically on the progress of this effort to ensure smooth transition into their programs. It is fully anticipated that the technology developed under this effort will be directly applicable toward other organic contaminants that are a major concern of these agencies. Once the pilot studies at the explosives contaminated sites have been completed, additional partnering with these agencies can be initiated for evaluation of peroxone for treatment of groundwaters contaminated with other organic compounds such as chlorinated solvents, fuels, and wood preserving wastes using the WES POPS unit.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	570	950	950	2470
WES	400	350	100	850
CRREL	200	200	50	450
AEC	0	150	0	150
USN	0	0	0	0
COE-MRD	0	0	0	0
TOTAL	1170	1650	1100	3920

12. Performers:

The WES will have the technical lead on this project. The US Army Engineer Cold Regions Research and Engineering Laboratory (CRREL), Dr. Tom Jenkins, will provide chemistry expertise toward identification of potential intermediates of incomplete oxidation. Mr. Ted Streckfuss, US Army Corps of Engineers-Omaha District and Mr. Lindsey Lien, COE-Missouri River Division, will develop a process design package and provide design concern input to ensure that the products of this effort can be easily utilized by and are of benefit to the user community. Messrs. Randy Cerar and Richard O'Donnell, US Army Environmental Center (AEC), will assist WES with the Army facility pilot study(s). Ms. Carmen Lebron, US Naval Facilities Engineering Services Center (NFESC), will also participate in this study by assisting WES in performing a pilot study at a Navy Site.

13. Principal Investigator:

Mr. Mark E. Zappi, P.E.
Environmental Engineering Division (EE-R)
USAE Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, MS 39180
PHONE: 601-634-2856
FAX: 601-634-3833

14. Keywords:

Peroxone, explosives, groundwater, advanced oxidation processes, pilot study, oxidizers

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Aerobic Bioremediation of a Contaminated Aquifer

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Lab

5. **Proposal ID:** #095

6. **Problem Statement:**

In situ bioremediation of fuels requires adequate nutrient and electron acceptor addition to enhance natural biodegradation. Current methods of in situ biological treatment often fail to provide adequate electron acceptor to metabolize fuel contaminants in groundwater. Problems with the rapid decomposition of hydrogen peroxide, nutrient-induced plugging, and poor oxygen distribution have all been documented in previous field studies. This is a continuation of a FY93 SERDP funded project.

7. **Project Description:**

This project will demonstrate novel methods of introducing nutrients and oxygen (or another suitable electron acceptor) into an aquifer contaminated with jet fuels. The approach will be to use lab testing (if recommended by review panel) to develop improvements to nutrient formulations and new methods of providing an electron acceptor in situ. Field studies will be performed utilizing in situ monitoring systems to provide real-time measurement of CO_2 production by microbes, in situ oxygen levels, and contaminant removal. The project will be composed of 3 tasks: task 1 will be an expert panel meeting to review the state-of-the-art and define promising ideas yet to be field tested; task 2 will be the development of a nutrient/electron acceptor delivery system controlled by in situ monitors; task 3 will be the successful pilot-scale test the integrated system which can monitor and feed back information on subsurface environmental conditions so an in situ bioremediation technology can be run in the most effective manner. This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.J: Treatment of Fuels in Groundwater.

8. **Expected Payoff:**

These improvements to in situ biodegradation will provide Air Force and DoD engineers with a more reliable and less expensive alternative for removing fuels from groundwaters.

9. **Milestones:**

1.	Expert Panel Meeting	01/94
2.	Site Selection	07/94
3.	Characterization of Site	09/94
4.	Develop Nutrient/Electron Acceptor Delivery System	11/94

5. Installation of Delivery System in the Field 01/95
6. Operation of System for 1.5 Years 06/96
7. Final Report 08/96

10. Transition Plan:

This project will transition to the Air Force Environmental Systems Program Office (HSC/YAQ) and the Air Force Center for Environmental Excellence (AFCEE/ES) for full scale remediations and finalization of the technical data package. A preliminary Principles of Practice Manual, Technical Reports and professional publications will be produced for distribution to all DoD IRP offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
PE63723F	82			82
SERDP	400	630	420	1450
TOTAL	482	630	420	1532

12. Performers:

The Environics Directorate of Armstrong Laboratory will coordinate this research with the EPA's Robert S. Kerr Environmental Research Laboratory and the Risk Reduction Engineering Laboratory.

13. Principal Investigator:

Catherine Vogel
AL/EQW
7139 Barnes Dr., Suite 2
Tyndall AFB, FL 32403-5323
TEL: (904) 283-6035
FAX: (904) 283-6090

14. Keywords:

Aerobic, Bioremediation, In Situ, Fuels, Hydrocarbons, Biodegradation

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Cleanup

2. Title: Air Waste Stream Treatment Technologies

3. Agency: Air Force

4. Laboratory: McClellan AFB

5. Proposal ID: #131

6. Problem Statement:

With the passage of the Clean Air Act, development of acceptable technologies for remediation of air waste stream has become an urgent issue. At McClellan, installation of a remedial action (e.g., Soil Vapor Extraction) was jeopardized because of a lack of acceptable air treatment technology. Most of the current technologies use incineration or activated granular charcoal to destroy or contain VOCs. Both the technologies are inefficient. Incineration produces a number of byproducts (e.g., HCl, NOx, etc.), while charcoal is ineffective with a number of contaminants, such as vinyl chloride. In a number of cases, the base's mission is jeopardized because of the air quality issues.

This project is in the technology demonstration and transfer category.

McClellan was selected as Tri-Services National test site for chlorinated solvents remedial technologies. Air Waste Stream treatment technologies need to be tested and developed at McClellan as there is a great need for these systems across DoD.

7. Project Description:

At McClellan, a number of remedial systems have been implemented that produce air waste streams. There are three pump and treat systems where water is air-stripped and VOCs are then incinerated. In addition, a soil vacuum extraction system has also been constructed and VOCs are then destroyed by catalytic oxidation. However, both systems produce unacceptable levels of NOx and HCl that is affecting the base mission capabilities. The current systems at McClellan produce a number of VOC in high concentrations in air phase. The compound detected are 1,1,1-TCA, 1,1-DCE, TCE, 1,1-DCA, C-1,2-DCE, Freon 113, Vinyl Chloride, Toluene, and Methylene Chloride at concentration of over 3000 ppm. Two air treatment systems are being considered for demonstration and development at McClellan. They are:

1) Air Biofilters: The system being considered uses bacteria to destroy the contaminants. The biofilter uses molded HDPE trays (covered with a patented media) in series to aerobically biotreat VOCs. The waste stream is mixed with non-chlorinated water to facilitate bacterial activity. This technology process was successful for petroleum hydrocarbon; however, it has to be developed for chlorinated solvents and 2) Photocatalytic System: The technology removes and destroys organic pollutants from air waste streams by using an illuminated titanium dioxide catalyst (Ti02-coated mesh). Photocatalytic reactor cells are arranged in series or parallel. The reactors contain a stainless steel jacket, a photocatalytic

matrix, and a lamp for illumination. The lamp emits low intensity ultraviolet light and is mounted coaxially within the jacket. A sleeve of fiberglass mesh coated with Ti02 is wrapped around the lamp. The Ti02 catalyst is activated by the light to create hydroxyl radicals which break down the organic molecules. Air flows into the reactor and passes through the catalyst matrix.

The remedial systems are McClellan AFB are designed to facilitate testing of these technologies. These will be attached to current systems through slip stream.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: 1.I: "Treatment of Solvents in Groundwater; 1.M: Treatment of Solvents in Soils and 1.N: Treatment of Fuels in Soils.

8. Expected Payoff:

Currently, pump and treat are perhaps the most widely used groundwater treatment technologies available. The insitu bioremediation is an extremely cost effective clean alternative that will reduce the risk quickly. In addition, it has wide applicability across the country.

9. Milestones:

1. Review Site Data	06/93 (Done)
2. Write Test Plan	09/94
3. Conduct Test - Technology 1 12/94 - Technology 2	03/95
4. Input from Industry	09/94 (Cont.)
5. Disseminate Information - Tech 1 05/95 - Tech 2	08/95
6. Final Report	12/95

10. Transition Plan:

McClellan, under EPIC, has set up a number of initiatives to transition the information generated by demonstration quickly to potential users. They are:

a. Greensheets: Information is sent out regularly to over 2000 people.

b. Public/Private Partnership: EPIC has an agreement with EPA (TIO & SITE) and seven private companies (AT&T, Monsanto, DOW, DuPont, Southern California Edison, Beazer, and Xerox) to jointly test and share cost and performance data of innovative remediation technologies.

c. National Test Site: McClellan was identified as a Tri-Services National Test Site for chlorinated solvent remediation technologies. The result from this demonstration will be transferred within DoD to potential users.

d. McClellan is proposing to be Western Governors' Association demonstration site and will be developing plan to help in the deployment and commercialization of the technologies tested at the site.

e. McClellan is proposing to enter in an understanding with the State of California where the technologies tested at McClellan will be jointly evaluated and "certified" by the State.

11. Funding: ($K)

	FY94
SERDP	700

12. Performers:

This will be a joint venture between McClellan, U.S. EPA (TIO, SITE, Region IX), Cal-EPA, EG&G, and Public/Private Partners.

13. Principal Investigator:

Bud Hoda
SM-ALC/EM
3200 Peacekeeper Way, Suite 11
McClellan AFB, CA 95652-1036
Tel: 916-643-1742 x 355
Fax: 916-643-0827

14. Keywords:

Air Waste Stream, Treatment, Chlorinated Solvents, VOC, Bioremediation, Photochemical Process.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Bioremediation of Hydrazine/Energetic Materials

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Lab

5. **Proposal ID:** #118

6. **Problem Statement:**

Current methods for disposal of highly energetic materials are open burn/open detonation, static firing, and incineration. These disposal processes produce significant quantities of air pollution and residual wastes. Recent restrictive regulations make these disposal options unacceptable. Also, impacts from past activities at energetic disposal sites must now be addressed. The current method for hydrazine spill decontamination is the addition of oxidizers which, in turn, produce hazardous conditions or more toxic contaminants in the environment. Treatment techniques need to be developed to replace existing disposal options and address environmental contamination from past disposal activities of these materials. Biological treatment techniques offer the most cost-effective alternative to meet these needs.

7. **Project Description:**

Advances in biotechnology and enzymology will allow for the exploitation of biological treatment for the degradation of hydrazine and other energetic materials. More specifically, recent successes in discovering the pathways involved in the metabolism of nitroaromatic compounds and ammonium perchlorate suggest similar techniques may be applied to hydrazine. The approach for the successful implementation of this biotechnology will involve process discovery, determination of limiting factors, process development, and scale-up of the biological system. This will include bench-scale testing to optimize the required biological systems to be followed by field testing of an appropriate bioreactor system at a contamination site. In accordance with DoD's Project Reliance, the Armstrong Lab's in-house 6.2 research will be transitioned to the Army Environmental Center (AEC) in FY95. The AF 6.2 research will generate biochemical and genetic information for pure microbial strains capable of completely biodegrading energetic materials. Ongoing work includes enzyme purification and pathway identification. Regulation mechanisms of pathways are also being studied. The final product of this research will be a thorough understanding of the molecular basis of the biodegradation which will allow us to extend the substrate range, alter the kinetics or regulation of the system, or otherwise improve upon the effectiveness of the process. This knowledge base will be transitioned to AEC to allow for scale-up of these biological systems. This knowledge base is crucial to fielding an efficient, optimized bioreactor system versus a 'black box' whose operation is not completely understood. The AF would collaborate during AEC's scale-up work in terms of providing scientific guidance in the areas of microbiology, biochemistry and genetics of the cultures/microorganisms. This will allow for the development of a properly designed reactor that will provide the microorganisms all necessary physiological requirements. This project

directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.G: Treatment Technology for Explosives in Groundwater, also Requirement Thrust 1.K: Treatment Technology for Explosives in Soils.

8. Expected Payoff:

Development of alternative disposal procedures, and understanding the fate of material already released into the environment is critical to maintaining compliance with the 1990 Clean Air Act Amendments (CAAA), the Federal Water Pollution Prevention and Control Act 1987 (FWPPCA), the Federal Facility Compliance Act 1992 (P. L. 102-386), and Executive Order 12865 (Aug 1993)/Federal Compliance with Right-To-Know Laws and Pollution Prevention Requirements. This project will produce a cost-effective, more efficient, destructive process to remediate sites contaminated with hydrazine and other energetic compounds within the regulatory requirements.

9. Milestones:

1.	In-House Literature Evaluation and Review (Hydrazine)	10/94
2.	Transition of Nitroaromatic Prototype to AEC	01/95
3.	Identify Microorganisms for Hydrazine Degradation	02/95
4.	Perform Bench-Scale Testing	04/95
5.	Develop Pilot-Scale Bioreactor System	04/97
6.	Field Testing Complete	02/99
7.	Report Results	04/99

10. Transition Plan:

This project will transition to the Air Force Environmental Systems Program Office (HSC/YAQ), the Air Force Center for Environmental Excellence (AFCEE/ES) and the Army Environmental Center for fielding of a remediation unit and finalization of the technical data package. A preliminary Principles of Practice manual, technical reports and professional publications will be produced for distribution to all DoD IRP offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	420	1140	1524	998	525	4607
TOTAL SERDP	420	2140	2524	998	525	6607

12. Performers:

This effort will be performed by the Environics Directorate of Armstrong Laboratory (AL/EQ), the Occupational and Environmental Health Directorate of Armstrong Laboratory (AL/OE), and the Army Environmental Center (AEC).

13. Principal Investigator:

Alison Thomas
AL/EQW
139 Barnes Dr., Suite 2
Tyndall AFB, FL 32403-5323
TEL: (904) 283-6028
FAX: (904) 283-6090

14. Keywords:

Bioremediation, Bioreactor, Energetics, Hydrazine, Nitroaromatic, Biodegradation.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Catalytic In Situ Treatment of Chlorinated Solvents

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Proposal ID:** #107

6. **Problem Statement:**

Organic liquids, such as chlorinated solvents, nonchlorinated solvents, and fuels, have been used in massive quantities over the last four decades. Release of these liquids to the environment accounts for a significant portion of environmental contamination requiring cleanup. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. There is a comparable degree of contamination at DOE and private Superfund sites.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground water quality. The technology chosen at over 90 percent of the sites with contaminated ground water is extraction followed by surface treatment. This technology, commonly known as pump-and-treat, contains contaminant plumes and removes dissolved-phase contamination in relatively homogeneous geologic formations. As a result of the slight solubility of the contaminant into the surrounding groundwater, and sorption to aquifer materials during transport, pump-and-treat processes require the treatment of massive amounts of water to remove relatively little contamination. Estimates of the duration of pump-and-treat necessary to fully remediate contaminated sites range from decades to centuries.

The high cost of pump-and-treat technologies are due to operations and maintenance costs, including energy for pumping and water decontamination, materials for treatment, and labor for constant operation of the process. A newly-developed process, called funnel-and-gate, is an in situ technique which directs contaminated groundwater under passive flow through an engineered subsurface region for decontamination. While this process may not reduce the duration of treatment, once installed, it will operate with little or no operating and maintenance (O&M) investment, resulting in considerable savings over the life of the project.

The best test of this technology will be in a well-characterized aquifer, treating a well-characterized plume. An accurate mass balance can be obtained only when the plume results from a controlled release of pollutant. The Air Force was recently awarded a SERDP grant to construct just such a controlled release site, which will be used for this demonstration. The groundwater can be decontaminated by a number of chemical, physical, biological, or a combination of methods. Existing research projects at both Armstrong and Athens (EPA) Laboratories have identified treatment methods which are well suited to funnel-and-gate deployment.

7. Project Description:

The funnel-and-gate consists of low hydraulic conductivity cutoff walls with gaps that contain in situ reactors (such as reactive porous media), which remove contaminants by abiotic or biological processes. The cutoff walls (the funnel) modify flow patterns so that ground water flows primarily through high conductivity gaps (the gates). Ground water plumes are thus directed through the in situ reactors in the gates where physical, chemical or biological processes remove contaminants from ground water. Remediated ground water exits the downgradient side of the reactor.

This applied research program will develop guidance on the use of funnel and gate systems containing various reactive media to treat chlorinated solvents in groundwaters. Studies will address two critical unknowns: 1) hydrogeologic uncertainties that have led to at least one failure of the technology, and 2) chemical reactions between reactive media and contaminants that lead to better designs. These studies will lead to a rigorous pilot-scale field demonstration to prove the technology.

An understanding of site-specific hydrogeology is critical to the design of funnel and gate systems. Groundwater flow rates and pathways must be known to position gates and to design the amount of reactive media required. New or improved groundwater flow and transport models will be developed to ensure that designers understand the system they will treat.

The proposed research will apply hydrogeological principles and aquifer modeling techniques to develop the most efficient designs and methods for construction of the walls. An increased understanding of groundwater flow through the engineered systems will allow for the most frugal emplacement while ensuring complete capture of the contaminant plume. The proposed work will develop new (or modify existing) three-dimensional groundwater flow models to simulate the flow of groundwater and contaminant plumes through aquifers modified with a funnel and gates. Of particular interest will be the influence of aquifer heterogeneities and site characterization. Variables to be examined will include size and shape of the funnels, requirements for wall integrity, number and placement of gates, and groundwater velocity through the gates. New modeling techniques will be developed to account for effects like aquifer clogging by iron bacteria. The models will be verified in field demonstrations using non-hazardous tracers to monitor groundwater movement through the system.

Concurrently, gate technologies will be designed and scaled for use with funnel-and-gate configurations. Environics Laboratory has for several years been investigating abiotic dechlorination in order to develop in situ treatment processes. Other research has been directed at contaminant mobility reduction using surfactants, a process which may enhance biological treatment in gates. The Environmental Research Laboratory at Athens has been studying abiotic dechlorination using elemental iron, enhanced with sulfur compounds, as an in situ process. All of these processes can potentially be used as gates to treat groundwater contaminated with chlorinated solvents. The elemental iron/sulfur catalytic dechlorination system developed by the Athens Laboratory is proposed as the first demonstration gate. Regardless of the nature of the gate, pathway analyses must be conducted in the field and laboratory, not only to predict residual toxicity, but also to aid in deriving the optimum design configuration. Mass accounting must be fully balanced to ensure complete destruction of the contaminant. Where necessary, labeled compounds and tracers will be

used. By coordinating the hydrogeologic modeling project with further development of the gates, a fully integrated system can be installed and tested in the field.

Failure of innovative technologies at a regulated site would result in wasted cleanup dollars and may actually complicate subsequent cleanup. Proving technologies in a well-controlled, isolated site will limit the risk and possible damage resulting from failure.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.I: Treatment Technology for Solvents in Groundwater.

8. Expected Payoff:

Most contaminated sites currently undergoing pump-and-treat remediation are expected to be tractable to funnel and gate configurations. Installation of passive treatment zones will save on O&M costs for what will likely be decades of continued treatment. With no active pumping involved in the process, these systems may be installed at sites for which power utility installation is a formidable obstacle to installation of pump-and-treat systems.

9. Milestones:

1.	Report on the mass balance of iron/iron sulfide reaction	08/94
2.	Develop computer model(s)	09/94
3.	Apply computer models to predicting modified hydrology	03/95
4.	Guidance documents on designing funnel and gate systems	06/95
5.	Report on the dehalogenase enzyme reaction and plant sources	09/95
6.	Design funnel-and-gate hydrology demonstration(s)	10/95
7.	Construct field demonstration	03/96
8.	Collect and analyze operational and monitoring data	09/97

10. Transition Plan:

The reports and guidance documents resulting from this work will be written so that they will be suitable for planning implementation at scales larger than the field studies of this project. The Air Force Environmental Systems Program Office (HSC/YAQ) and the Air force Center for Environmental Excellence (AFCEE/ES) will further develop the technical information obtained from this research and apply it to full scale remediations and finalization of the technical data package. A preliminary Principles of Practice Manual, Technical reports and professional publications will be produced for distribution to the appropriate technology transfer offices of the Air Force, Army, Navy, DOE, and EPA.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	720	890	950	850	3410

12. Performers:

The performers for the proposed work are US Air Force Armstrong Laboratory, Environics Directorate (AL/EQW), the EPA Environmental Research Laboratory at Athens, and the University of Waterloo, Waterloo, Ont, Can.

13. Principle Investigator:

Major Mark H. Smith, PhD
AL/EQW-OL
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
Phone: (904) 283-6126
Fax: (904) 283-6286

14. Keywords:

Funnel and Gate, Remediation, Cleanup, Aquifer, TCE, Chlorinated Solvents

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Joint US/Germany In-Situ Bioremediation Demonstration

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Proposal ID:** #099

6. Problem Statement:

The goal of this effort is to conduct a field demonstration of bioventing concurrent with two groundwater treatment strategies at a JP-4 jet fuel contamination site at Rhein Main AB, Germany. The results generated from this field project will assist in successfully transferring these technologies to the German regulatory authorities and the German environmental consulting firms working on U.S. military base cleanup activities in Germany.

There are approximately 2,000 fuel/hydrocarbon contamination sites the US Air Force must address in it's Installation Restoration Program. There are also numerous such sites at military facilities throughout Germany and other NATO countries. Any in-situ method for soil or groundwater cleanup will offer huge cost savings over the currently used ex-situ disposal or treatment methods.

This effort represents an enhancement to several existing programs: "Bioventing for In-Situ Cleanup of JP-4 Contaminated Soils," "Anaerobic Degradation of Fuel-Contaminated Groundwater," and "Natural Attenuation."

7. Project Description:

The technical objective of this effort is to demonstrate bioventing for the cleanup of JP-4 contaminated soil located beneath the taxiway at Rhein Main AB Germany. To improve the effectiveness of bioventing, the "bioslurper system" will also be demonstrated to remove free product from the site prior to bioventing. Specific tasks are outlined below. The rationale for using natural or enhanced attenuation to address the contaminated groundwater will also be tested at a separate JP-4 contamination site at Rhein-Main AB.

The technical approach will include a field demonstration site to allow for the testing outlined above has been selected at Rhein Main AB. Construction of the experimental plots/areas and outfitting with the necessary hardware and monitoring equipment will be accomplished jointly by the University of Karlsruhe and an AL/EQ contractor. The mechanism which facilitates this collaboration is the DoD's US-German Data Exchange Agreement. Both the University of Karlsruhe and AL/EQ's technical objectives will be accomplished at this field site. This will be a three-year demonstration.

The tasks to be accomplished are as follows. The primary party responsible for accomplishing the tasks is noted in parentheses:

- Construction of treatment cell (GE)
- Perform experiments to better define mass balance and monitoring methods (primarily US with some GE involvement)
- Testing methods to improve biodegradation rates (GE)
- Testing methods to improve application of bioventing such as bioslurper (US) and surfactants (GE)
- Nitrate enhancement for groundwater treatment (GE)
- Natural attenuation (US)
- Sampling/Monitoring/Analysis (US + GE)

This work will assist the DoD in achieving its Year 2000 cleanup goals and also be applicable to similar fuel contamination sites on DOE facilities. The proposed effort relates closely to AF, Navy, and EPA's previous and ongoing work in bioventing. AL/EQ and the US Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory are also currently involved in development of nitrate enhancement for groundwater decontamination as are a few select researchers in Germany. Lastly, the AF is involved in a collaborative effort with TVA on a natural attenuation demonstration.

The technical risk is medium. This judgment is based not on the feasibility of bioventing or the other technologies to be tested, but on the fact that they are to be tested on contaminated soil lying beneath an active taxiway.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1N: Treatment of Fuels in Soils.

8. Expected Payoff:

The bottom-line payoff is that these very low-cost technologies will save the US and German governments millions of dollars per contaminated site over conventional cleanup technology. The key outcome of this joint demo will be performance and cost information to convince the German regulatory authorities that bioventing/bioslurper/natural attenuation are viable treatment options for hydrocarbon contaminated aquifer material. We will also identify the operating difficulties associated with attempting these technologies beneath an active taxi way (8-10 inches concrete). Lastly, the two bioremediation technologies, independently developed by the US and Germany, could be enhanced as a result of this joint effort.

9. Milestones:

1.	Draft Treatment Study Test Plan	11/94
2.	Final Treatment Study Test Plan	12/94
3.	Draft Quality Assurance Project Plan	12/94
4.	Final Quality Assurance Project Plan	01/95
5.	Construction of Experimental Field Plots	03/95
6.	Completion of Bioslurper Experiments	07/95
7.	Completion of All Field Experiments	10/97
8.	Draft Technical Report	10/97
9.	Final Technical Report	12/97

10. Transition Plan:

Technical results from this demonstration will be transferred via interim reports throughout the life of the project, final technical report, and design guidance. Design packages, technical data, and operator manuals will be available and will be transitioned to the Air Force Environmental Systems Program Office (HSC/YA), the Air Force Center for Environmental Excellence (AFCEE) for development and fielding, and will be distributed to all DoD IRP offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

The users (contracting and consulting firms such as Battelle) will be the performers. The main coordination needed will be with the German regulators to keep them informed of the project's progress. The industries ability to assume production is high.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	450	200	300	950

12. Performers:

The project will be jointly managed by the Environics Directorate of Armstrong Laboratory (AL/EQ) and the German BWB through our existing Data Exchange Agreement. It will be performed by a qualified AL/EQ contractor and the University of Karlsruhe, Germany. No CRADAs are anticipated.

l3. Principal Investigator:

Catherine Vogel, Project Manager
AL/EQ-OL
139 Barnes Drive, Suite 2
Tyndall AFB FL 32403-5323
TEL: (904) 283-6035
FAX: (904) 283-6090

14. Keywords:

Bioremediation, Natural Attenuation, Bioventing, Remediation, Cleanup, Nitrate Enhancement

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** In-Situ Chemical Treatments for Enhanced Subsurface Cleanup

3. **Agency:** DOE

4. **Laboratory:** Lawrence Livermore National Laboratory (LLNL)

5. **Proposal ID:** #430

6. **Problem Statement:**

6.1 Goal: The goal of this project is to develop the technology and demonstrate through field tests an integrated suite of novel chemical processes for rapidly and cost-effectively remediating subsurface contamination in the groundwater and vadose zones by fuel hydrocarbons (FH), chlorinated solvents (CS) and toxic metal ions (TMI). The specific chemical processes to be developed and demonstrated in the field under this proposal, as both separate and combined processes, are:

1. Accelerated decontamination of fine-grained sediments (FGS): Increasing the permeability of FGS by injection of slugs of selected non-toxic organic solvents (OS) (e.g., ethanol (ETOH) in high concentrations and/or cationic flocculants (CF) (e.g., aluminum hydroxide) in moderate concentrations.

2. Accelerated contaminant removal by solvent washing: Enhanced mobilization and extraction of contaminants either sorbed, or dissolved in groundwater, by injecting slugs of OS.

3. Chelate-mediated removal of TMI: Enhanced mobilization and removal of TMI by injection of non-toxic chelates (e.g., DMSA).

4. Creation of in-situ contaminant containment barriers: Methodology for the creation of in-situ chemical treatment compartments at both shallow and deep sites through surface accessed and borehole accessed operations.

6.2 Relevance: Massive quantities of TMI and hydrophobic organics such as FH and CS have been released into the subsurface at over 1000 DoD sites. These compounds are found dissolved in the groundwater, dispersed in vadose-zone air, in free-product form (i.e., as non-aqueous-phase-liquids or NAPLs), as material sorbed on solid phases. Remedial technologies developed to date to remove these contaminants have proven to be either too slow or too costly for restoration of heterogeneous sites.

The slow release of contaminants from FGS due to their low-permeability and high-sorptivity, the inability of groundwater, vadose-zone air and externally injected fluids to adequately access and flush these sediments, and the low-solubility and low partitioning of hydrophobic contaminants in water, are the primary factors that seriously limit the effectiveness of nearly all remediation processes that are either currently in use or are being developed. In highly heterogeneous formations, the great disparity in permeability between

FGS and coarse-grained sediments (CGS) causes flow channelling and confinement of the flushing action of induced water and air flows to the CGS, thus bypassing the FGS. At the conclusion of pumping, the slow egress of contaminants from the FGS into the previously cleaned CGS recontaminates the fluids and sediments in the CGS. As a result, site restoration to stringent regulatory groundwater quality standards by any method, such as pump-and-treat (P&T) or vacuum venting, that does not overcome these limitations, often takes too long (decades) and costs too much (millions of dollars) to achieve. Recognition of the pivotal roles these phenomena play in limiting the effectiveness of existing remediation methods has led us to develop the chemical treatment processes we propose here. If these processes are successfully developed and demonstrated, then they can be deployed either as stand-alone processes, or as pretreatments for other methods to devise highly effective hybrid processes. We estimate that, for a typical cleanup, an order of magnitude reduction in remediation time and a very substantial reduction in remediation cost would result from successful application of these chemical treatment methods.

6.3 Research category, project history and previous funding: This work is proposed under the SERDP Applied Research/Technology Demonstration/Technology Transfer (6.2/6.3) Project Selection Criteria category. The proposal consists of both new work and enhancements to previously funded projects. Enhancing the permeability of FGS through the use or organic solvents and cationic flocculants, and the use of OS soluble chelating agents for TMI recovery, are new concepts developed at LLNL. Solvent washing to enhance contaminant removal is currently being jointly developed by the Robert S. Kerr Environmental Research Lab (RSKERL) and the USAF Armstrong Lab, Environics Directorate (AL/EQ), Tyndall AFB, FL. Also, with funding from DOE's ERWM program, Lawrence Berkeley Lab (LBL) is developing methods for creating in-situ containment walls, Thus, the requested SERDP funds will leverage existing programs to provide a broader base for national implementation of the new remediation technologies proposed here. While the USAF program and the AL/EQ are focused on meeting DoD's specific needs, the results of this project would benefit DoD, DOE, EPA and the remediation industry.

7. Project Description:

7.1 Technical objective: The principal objective of this research is to develop and demonstrate through field tests an integrated suite of chemical treatments for enhancing P&T methods in a variety of geologic settings. The desired and result of the work is to produce guidance documents and design tools for applying these processes to remediate subsurface contamination by FH, CS and TMI. The guidance will address all aspects of the remediation effort including field characterization, laboratory experimentation, computer modeling, process design, and cost analyses to achieve the maximum benefit from the proposed cleanup processes.

7.2 Technical approach: The proposed work will consist of an initial technology development phase followed by a series of field demonstration tests of enhanced P&T methods. In the technology development phase, constitutive experiments will be undertaken to ensure 1. the effectiveness of highly concentrated OS and moderately concentrated CF in enhancing the permeability of FGS under confining stresses typically found at these depths, 2. the enhanced solubility and partitioning of dissolved and adsorbed phase contaminants in the solvent, and 3. the mobilization of TMI by chelates. In addition, bench scale experiments will be performed 4. to verify the design of the unit processes required to sepa-rate the contaminants and solvents from the effluent stream at the surface, to evaluate 5. the impact

of the chemicals injected underground on indigenous biota and 6. the potential for in-situ anaerobic conversion of ethanol to methane. Subsequently, flow and tracer transport experiments impact of 7. slug dilution, 8. solvent front stability, 9. aqueous chemistry and 10. media heterogeneity on the effectiveness of the chemical treatment processes.

Successful completion of the technology development phase will enable us to make the decision to proceed with two field demonstration tests. these two tests will be performed in both the groundwater and the vadose zones at two field sites with different geohydrogical and geochemical characteristics. The first test will be performed at a site containing thin streaks composed primarily of impermeable FGS embedded within relatively permeable formations extending into both the groundwater and vadose zones. The second test will be performed at a site containing relatively continuous, homogeneous and monolithic fine-grained formations adjoining permeable coarse-grained formations. These characteristics represent two limiting geohydrologic regimes commonly encountered in subsurface remediation. However, the final site selection will depend on the availability of suitable test sites. With the test sites selected, we will undertake site characterization, site-specific treatability tests, 3D flow, predictions, and post-test performance evaluation.

In all of these treatment processes, to minimize the cost of chemicals, we reduce the amount of chemicals used by driving chemical slugs of finite width through the target zone ahead of an inexpensive bank of water. The chemical slug is preceded and followed by pre- and post-buffer slugs of finite widths. These buffer solutions contain additives to condition the formation and to stabilize the slug against premature hydrodynamic breakup and dilution. Similar concepts have been utilized by the oil industry for enhanced oil recovery by solvent flooding. In our field tests with FH and CS contaminants, the main chemical slug will always contain the OS, and may or may not contain CF depending on the site conditions and the specific process being studied. The pre-buffer may contain dilute solutions of OS and/of CF while the post-buffer will contain viscosity modifiers for stabilizing the trailing edge of the slug against breakup. In those field sites contaminated by TMI, the pre-buffer will contain custom-designed, TMI-specific chelates to mobilize the contaminant which will then be removed to the surface.

Studies on the mechanism of permeability enhancement by OS have been reported in the literature in the context of punch-through leakage of OS from clay-lined waste retention ponds. We have capitalized on this phenomenon, that is disastrous in clay-liners, to extract a tremendous increase in the speed with which contaminants can be coerced from FGS. This permeability enhancement results from the collapse of the electrical double layer that maintains clays in the swollen state. Collapse of the double layer and the resulting decrease in the volume of clay is effected by introducing OS to lower the dielectric constant of the fluid phase. This collapse induced the formation of cracks in the FGS; making the interior regions of the FGS accessible to the washing fluid, and permitting the rapid mobilization and egress of contaminants out of the FGS. When ETOH is the washing fluid, there is also the advantage that the hydrophobic contaminants become miscible or highly soluble, and thus promote contaminant desorption. The contaminated ETOH-water mixture will be pumped to the surface by an extraction well. The effluent will then be filtered to remove soil particles, passed through adsorption columns to remove the TMI and hydrocarbon contaminants, and further processed by distillation and molecular sieving to separate the water from the ETOH. The purified and concentrated ETOH will be reinjected to continue the process cycle. The treatment zone will be enclosed both vertically and horizontally by flow barriers to isolate it

from its exterior environment; this enclosure also permits the remediation of the vadose zone using buffered vertical floods.

7.3 Tasks: The project tasks are: 1. Process development lab tests, 2. Site selection and characterization, 3. Treatability lab tests and process design, 4. Predictive process simulations and economic analyses, 5. Field test implementation, monitoring, and data acquisition, 6. Performance evaluation and reporting.

7.4 Technical feasibility and risk: The feasibility of our chemical remediation approach depends on the effectiveness and cost of chemicals, the degree of dilution and stability of the chemical slugs in the subsurface, the aqueous geochemistry and sediment composition, the ability to recover, decontaminate and recycle the injected chemicals, and the potential toxicity of the chemicals to biota. Of these, the greatest uncertainty is introduced by subsurface heterogeneity. Currently, ethanol is not listed in EPA's Drinking Water Standards as a hazardous material. The technical risks are reduced by the wealth of available knowledge on chemical flooding techniques in the oil industry, the demonstrated permeability enhancement in clays by OS and CF, and the chemical engineering unit processes of contaminant separation and recovery. The program of lab experiments and modeling studies we propose to undertake in this project is designed to further reduce the risk of failure.

8. Expected Payoff:

Existing P&T methods are ineffective and are mainly used for hydraulic containment of contaminant plumes. Our process, especially when embedded in a hybrid process, could greatly reduce the treatment time and cost of cleanup, especially in heterogeneous environments. Through careful and detailed documentation, and continuing assistance form the project participants, the results can be transferred to industry for applying and commercializing this process.

9. Milestones:

1.	Initiate process development lab tests	10/94
2.	Initiate process and cost model development	10/94
3.	Initiate 1st field site selection	02/95
4.	Select 1st test site, start site characterization, treatability tests and process design	05/95
5.	Initiate 1st field test	12/95
6.	Complete 1st field test	10/96
7.	Initiate 2nd field site selection	01/97
8.	Select 2nd test site, start site characterization, treatability tests and process design	03/97
9.	Complete 1st field test analysis and reporting	06/97
10.	Initiate 2nd field test	07/97
11.	Complete 2nd field test	05/98
12.	Complete 2nd field test analysis and reporting	09/98
13.	Complete final project report and design manual	09/98

10. Transition Plan:

The technology which will be developed within this project will be transferred via lab reports, journal papers, design manuals and computer programs. j We are currently evaluating industrial firms for collaboration in this project. Groundwater Technologies, Inc. (GTI) of Trenton, NJ has written a letter of intent to enter into a cooperative research and development agreement (CRADA) with LLNL if this proposal is funded.

11. Funding: ($K)

FY94	FY95	FY96	FY97	FY98	TOTAL
0	2105	4450	4905	1675	13135

12. Performers:

The lead lab will be LLNL (permeability enhancement, chelates, process design, process and cost modeling, effluent treatment). The other participating institutions are: US-EPA RSKERL (co-solvency, biota, process modeling); LBL (polymeric barriers); USGS (field measurements); USAF AL/EQ (site selections); GTI (process design, field demo, commercialization).

13. Principal Investigator:

Edward J. Kansa, PhD
Lawrence Livermore National Laboratory
P.O. Box 808, Mail Stop L-200
Livermore CA 94551
Tel: (510) 423-0151
Fax: (510) 423-6907

14. Keywords:

subsurface cleanup, solvents, flocculants, chelates, ethanol.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** The Engineering Design of In Situ Bioremediation

3. **Agency:** Department of Energy

4. **Laboratory:** Idaho National Engineering Laboratory

5. **Proposal ID:** #514

6. **Problem Statement:**

In situ bioremediation (ISB) has been used successfully for two decades for the restoration of soils and groundwater contaminated with hydrocarbons. ISB is more environmentally sensitive and less expensive than more invasive alternatives (e.g., excavation, incineration). In addition, it acts as a useful complement to other in situ technologies such as air-stripping (vapor vacuum extraction and groundwater sparging), hydraulic containment and pump and treat. Recently attempts have been made to apply ISB to situations that are more microbiologically complex, including; contaminants present at elevated concentrations that inhibit microbial growth, contaminants (like explosives) that can only be completely mineralized by a consortia of microorganisms and contaminants like the chlorinated solvents that are not a carbon/energy source for bacteria but can be degraded through cometabolic pathways. Results from these projects have often been disappointing.

The basic hypothesis of this proposal is that the variable record of ISB is due to the lack of a consistent engineering design process. The input to this process would be all the site-specific geochemical, hydrological and microbiological data that can be gathered with reasonable expenditure of time and money. It's output would consist of:

- A statement of whether ISB can achieve compliance with the applicable regulations (i.e., drinking water standards, etc.).

- A decision about how ISB can best be combined with other contaminant-removal technologies.

- A design and control scheme specifying close-to-optimum values for process variables (i.e., well types, flow rates, composition of the injected nutrient stream, etc.) and how they should be varied over the life of the project.

The objective is field-scale ISB projects that can be turned on and left to run with confidence. Once the design and control strategy have been established, major changes should be unnecessary. It may be argued that treating ISB as a "Field-Scale Experiment" is an opportunity to learn something new. To the engineer, any such need to manipulate process variables once the process has begun is an expensive admission of the failure of the design process.

The author's experience suggests several reasons for the lack of a clear-cut design procedure. First is the shortage of process variables. The designer of a surface bioreactor is free to pick

the type and size of reactor, to control the pH and to include agitation and/or cell recycle to mix the bacteria, nutrients and contaminants together. The ISB designer tries to achieve the same ends by varying only the flow rate and composition of the injected nutrient stream. Second, some of the tools of engineering design are difficult to apply to ISB. What, for example, does "scale-up" mean at an ISB site with no natural boundaries? Similarly, experience is a valuable tool for designing traditional processes such as sewage treatment because municipal sewage varies little from town to town. However, the performance of ISB is so site-specific that experience gained at one site may not be transferable to the next. The third reason is the sheer complexity of the underlying phenomena of ISB. These include, the details of the hydrology, geochemistry and microbial metabolism as well as questions regarding the adsorption of contaminants and microorganisms to soil particles. In order to integrate the available information into a workable design, the details of all of these phenomena must necessarily be simplified. Unfortunately, such simplifications often lead to interdisciplinary disputes. For example, mathematical models are potentially valuable design tools but are often written by hydrologists with little knowledge of microbiology. Meanwhile, microbiologists conduct biodegradation experiments in such a way that critical modelling parameters can not be extracted from the results. Development of a standardized procedure would eliminate such confusion and keep all the relevant scientific and engineering disciplines working efficiently towards the good of successful ISB.

7. Project Description:

The ISB designer actually has two tools available; the mathematical model and experiments. The objective of this project is to show that best results are obtained only if these tools are properly integrated. The obvious, but often overlooked, requirement that no parameter be allowed into a model unless an experimental procedure exists to measure its value, automatically limits the complexity of the model. For example, there is little point in employing complex dispersion models if only simple tracer data will be available from the site. Similarly, designing the experiments so that their results can be translated into site-specific parameter values, maximizes their utility. This project involves three tasks; a) developing design models with appropriate levels of complexity, b) designing treatability experiments so that they provide data in a useful form, and c) transferring these procedures to the ISB industry.

a) Model Development

No one person will ever be sufficiently expert in all of the underlying phenomena of ISB to say whether it will achieve compliance at a particular site and how it should be designed and controlled. A mathematical model is an essential repository for the combined quantitative knowledge of many specialists. Such a model can be used to test different combinations of the process variables (well location, nutrient concentration, etc.) and to select the best combination. It can also provide the best prediction of the outcome of the process and suggest a rational control strategy based on differences between model predictions and field measurements.

The difficulty with existing models is that by attempting scientifically-exact descriptions of all facets of the problem, they become too complex for use in process design. The overall problem is so complex that methods for separating what is truly important from the mass of detail must be employed. One such method is dimensional analysis, a valuable design tool that has yet to be applied to ISB. Another is the concept of the biologically-active zone (BAZ). As injected nutrients spread out from an injection well, they reach a point where their

flow velocity is small compared to the growth rate of the microorganisms. The BAZ is the region around the expanding nutrient front where the contaminant, the nutrient and the microbes are mixed together by the effects of dispersion and adsorption. If this zone is thin, considerable simplification of the mathematics (and thus of our quantitative understanding) is possible.

These methods will be explored by solving a series of well-posed model problems. For example, in a plume of a biodegradable contaminant at inhibitory concentrations in a two-dimensional confined aquifer where should nutrient injection wells be located in order to provide the fastest clean-up with minimum displacement of the contaminant off the site? Can this optimum positioning be related to other variables (dispersion coefficients, inhibition constants, etc.) by correlations of dimensionless numbers? Are solutions based on the BAZ concept adequate approximations to the complete solution?

b) Design of Treatability Experiments

Many workers seek to simulate ISB by constructing laboratory columns of aquifer material and flowing groundwater through them. While this approach provides some insight into the process it is impossible to determine the inherent kinetics for growth and degradation by the indigenous bacteria from such data (the reasons involve the form of the mass conservation equations for a column; 2-dimensional partial differential equations). Batch microcosm experiments have a different drawback. Fluid flow (even if only that caused by nutrient injection) is an essential part of ISB. Since there is no flow in a batch experiment, it is unlikely that phenomena like adsorption/desorption of microbes will be well-simulated in the experiment.

In previous work under the DOE Subsurface Science Program and the Non-Arid Lands Integrated Demonstration at the Savannah River site, the authors have developed a system called the Differential Soil Bioreactor (DSBR) which overcomes these difficulties. It consists of a disc-shaped element of soil through which groundwater is recirculated so that all of the microorganisms are exposed to the same physicochemical conditions. Further refinement of the experimental and data analysis procedures are needed to extend the range of sites to which this device is applicable. Also, a modified version of the DSBR will be designed and built to extend the concept to bioremediation in the vadose zone.

c) ISB Technology Transfer

Several companies have installed ISB operations. The type of treatability studies and design procedures they employ (at least those that have been published) show little consideration for the complex interactions between flow, dispersion, microbial attachment, contaminant adsorption, biodegradation, etc. that influence the outcome of ISB. During the first year of the project discussions of this problem will be conducted with these companies and EPA personnel responsible for treatability study procedures. Any company wishing to collaborate on the project will be included through the establishment of a CRADA.

8. Expected Payoff:

ISB has many potential advantages. It can treat many contaminants of interest to DoD including fuels, chlorinated solvents and explosives. It can treat large volumes of contaminated soils down to compliance levels at a much lower cost and less environmental impact then competing technologies. There are several variants of ISB including injection of liquid-phase nutrients into a contaminated aquifer, bioventing (passive ventilation of the

subsurface to minimize volatilization and maximize biodegradation), and horizontal wells for sparging gas-phase nutrients into contaminated groundwater. What they have in common is that they will only function properly if they are designed correctly, which means that the details of the process must be related to the geological, hydrological and microbiological characteristics of the particular site. Successful development of the procedure proposed here will remove many of the uncertainties presently associated with the application of this technology. It's benefits can then be employed with confidence at many DoD, DOE and private industrial sites.

9. Milestones:

1. Complete ISB site selection, preliminary characterization and establish industrial partnerships	03/96
2. Complete DSBR studies	12/96
3. Complete model for implementation of ISB	03/97
4. Complete status report of ISB industry	09/97
5. Complete ISB field study	09/98

10. Transition Plan:

The proposed combined modelling/experimental procedure will be tested and evaluated at a appropriate site during FY97 and FY98. Present candidate sites are severe solvent contamination problem at Hill Air Force Base Ogden, Utah and a Trichloroethylene problem in the groundwater in Pocatello, Idaho. The former would be performed in cooperation with the USAF and Montgomery Watson (currently contracted to provide restoration support). The latter is currently under study by CH2M Hill Co. with ISB as a possible remediation technology. Other sites will be selected in accordance with CRADA guidelines.

11. Funding: ($K)

FY94	FY95	FY96	FY97	FY98	TOTAL
0	290	340	340	290	1260

12. Performers:

The Office of Industrial Biotechnology and Process Engineering at the Idaho National Engineering Laboratory (INEL) is an interdisciplinary group of geneticists, microbiologists and bioprocess/environmental engineers, with considerable experience in environmental microbiology and bioremediation. It also maintains strong links with the geochemists and hydrologists at the INEL. The Principal Investigator and members of the proposal team have been involved in ISB research through the DOE/OHER Subsurface Science Program and the DOE/OTD Non-arid Lands Integrated Demonstration. Dr. Andrews also has served as Co-Chairman of a session on "Bioremediation of Soil" at the AIChE Annual Meeting in Los Angeles, November 1991; and a panel member for a workshop on "Bioremediation Research" at the AIChE Annual Meeting in Minneapolis, August 1992.

13. Principal Investigator:

Graham F. Andrews, PhD
Office of Industrial Biotechnology and Bioprocess Engineering
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-2203
Phone: (208) 526-0174
Fax: (208) 526-0828

14. Keywords:

soil, groundwater, in situ, bioremediation, bioreactor, solvents

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Aquifer Restoration by Enhanced Source Removal

3. **Agency:** EPA

4. **Laboratory:** RSKERL

5. **Proposal ID:** #368

6. **Problem Statement:**

The goal of this project is to provide field demonstrations of innovative processes to remediate aquifers contaminated by non-aqueous phase liquids (NAPLs) including fuels, solvents, and other organic contaminants in a timely and cost-effective manner. These demonstrations are targeted at DoD, DOE, EPA, their contractors, and other public and private organizations responsible for remediation of contaminated ground water. Low-solubility organics such as chlorinated solvents were used and released to the environment in massive quantities during the 1950's, 60's and 70's. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. At these sites the organic contaminants are found in one of three phases: (1) dissolved in the ground water (dissolved phase), (2) sorbed to the aquifer solids (sorbed phase), or (3) as a separate non-aqueous phase liquid (NAPL phase), all of which need to be removed if the ground water is to be restored to a usable quality.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground-water quality. For those contaminants that have found their way into ground water in the deeper subsurface, remediation technology options are extremely limited. The technology chosen at over 90 percent of ground-water contaminated sites is extraction followed by surface treatment. This technology, commonly known as *pump-and-treat*, has had some success in containing contaminant plumes and removing dissolved-phase contamination in relatively homogeneous geologic formations, but, as currently implemented, has not proved to be effective at restoring contaminated ground water to desired levels of cleanliness. The major limitations to the successful use of pump-and-treat are related to difficulties in extracting contaminants from the subsurface. Aquifer characteristics important in limiting the success of pump-and-treat include: (a) aquifer heterogeneity, (b) sorption of the contaminant to aquifer solids, and (c) the presence of a separate immiscible non-aqueous phase liquid (NAPL).

There is a particular need for enhancements to pump-and-treat technology that can overcome the limitations imposed by aquifer heterogeneity, sorption, and the presence of NAPLs. A number of enhanced pump-and-treat technologies have been proposed and demonstrated in the laboratory, but none have been subject to an objective field evaluation, nor is engineering design guidance available for routine application to contaminated ground-water remediation.

The EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL), through its subsurface cleanup and mobilization processes (SCAMP) program, and the Armstrong Laboratory, Environics Directorate (AL/EQ) at Tyndall AFB, FL, and both agencies through the SERDP program, have been working on innovative methods to increase the removal rates of toxic

organic compounds from the subsurface. This proposal is an enhancement to the programs of both institutions.

7. Project Description:

The objective of this research is to demonstrate processes for enhancing contaminant removal (enhanced pump-and-treat technologies) in a variety of geologic settings and to produce engineering design guidance documents for applying these processes to remediate contaminated ground water. The guidance will address the entire remediation effort, including site characterization and supporting laboratory work, required to achieve the maximum benefit from the remediation technologies included in the study.

The proposed work will be a series of field demonstrations at two or more sites of enhanced pump-and-treat technologies supported by site characterization and laboratory research required to produce a credible field demonstration and a credible evaluation. The work will focus on remediation of sites believed to be contaminated by non-aqueous phase liquids (NAPLs), such as chlorinated solvents. The proposal is to conduct these demonstrations at contaminated DoD sites to increase the likelihood that the results will be directly applicable to actual remediation projects.

The tests will be conducted as small-scale field projects. Each technology will be compared, at the same site, with several alternative remedial technologies including pump-and-treat. The results of these comparisons will show the differential improvement achieved by one process relative to another.

The proposed work will demonstrate and evaluate processes to enhance subsurface contaminant removal that are presently at a stage of development where they can be seriously considered for use in installation/restoration programs at DoD facilities. Such processes include innovative methods, such as: pulsed pumping, to optimize system design and operation for conventional as well as enhanced pump-and-treat; solvent flushing with water-miscible solvents such as ethanol; surfactant flushing; hot water flushing; and methods for forcing fluids through regions of low hydraulic conductivity.

Each evaluation will involve a set of similar tasks: site selection and characterization, design and construction of test facility, operation and monitoring, and evaluation and reporting. Each site will be characterized using state-of-the-art non-invasive and invasive techniques to provide the data necessary to select, design, operate and evaluate the remedial technology under study. Existing research design models will be utilized to develop the actual test facilities. The last part of each demonstration will be an evaluation of the test data and the preparation of a report. The report will describe site characterization, system design and operation, performance evaluation, degree of remediation achieved, cost analysis, factors limiting the success of the technology, and additional research, if any, required to overcome these limitations. These reports will form the basis for an engineering design guidance manual scheduled for completion 06/97.

The proposed work is a continuation of work performed under SERDP Phase I and Phase III and addresses Thrust 1I: Treatment of Solvents in Groundwater, and Thrust 1J: Treatment of Fuels in Groundwater under Pillar 1: Cleanup of the Tri-Service Strategic Environmental Quality Strategic Plan. The proposed work extends RSKERL's SCAMP research program, which is an effort to improve the efficacy of pump-and-treat remedial actions for ground water contaminated by chlorinated solvents. The proposed work complements the (AL/EQ) Small Business

Innovative Research (SBIR) and SERDP (Phase I) funding to encourage businesses to work on DoD environmental problems. A fully contained hazardous waste unit at Hill AFB has tentatively been selected as the first demonstration site. The selected site has a mixture of LNAPLs including: POLs, pesticides, PCBs and Dioxin. A small amount of the LNAPL is still mobile but the majority is now at residual saturation. Hydraulically, the site appears to be sufficiently permeable to permit delivery of the remedial fluid to the point of contamination. The contamination is sufficiently close to the surface to minimize construction cost. State and Federal regulators have been approached to obtain permission to make Hill a demonstration facility for extraction technologies. Site characterization is underway at Hill by the University of Florida to collect data needed to design the first co-solvent field study. EPA/RSKERL and AL/EQ both have strong laboratory and field programs directed toward in-situ remediation of contaminated ground water. The subsurface remediation expertise from these programs is available to provide support to the proposed work.

Each of the proposed processes has been shown to overcome some limitations that prevent remediation of contaminated aquifers. However, there are a number factors that have not been field evaluated. Three of these factors are: the high degree of spatial variability in the subsurface environment, the difficulty of obtaining in-situ mixing of a remedial additive with a subsurface contaminant, and changes in the hydraulic properties of the system as the NAPL is removed.

8. Expected Payoff:

Pump-and-treat systems are the primary technology in use at sites with contaminated ground water. Because of their inability to effectively clean up source regions of contaminated waste sites, many of them are being used primarily to provide hydraulic containment; and the forecasts are that they will need to be operated "in perpetuity." The proposed work will allow developing technologies to be implemented faster and with more confidence in their performance. The demonstrations will provide guidance in the application based on carefully documented field experience, which should, in turn, improve acceptance within the regulatory community. Estimated costs for ground-water remediation by DoD and other federal agencies range upwards of hundreds of billions of dollars, and even incremental improvements in efficiency will justify the costs of the proposed research.

9. Milestones: (* completed on schedule)

1.	Select site and technologies for first tests	10/93*
2.	Initiate site characterization	10/93*
3.	Construct treatment systems for tests	05/94
4.	Initiate first set of tests	06/94
5.	Select site and technologies for second test	09/95
6.	Write test report for first tests	01/96
7.	Construct treatment systems for second test	04/96
8.	Initiate second set of tests	05/96
9.	Write test reports	04/97
10.	Produce engineering design guidance report	06/97

10. Transition Plan:

The proposed work will consist of small-scale controlled field demonstrations. The reports and guidance documents resulting from this work will be written such that they will be suitable for full-scale planning and implementation.

The EPA/RSKERL Technology Support Center (TSC) has provided technical assistance on over 300 Superfund sites since 1987. RSKERL has an on-site professional staff with a primary responsibility for technical assistance. RSKERL has conducted numerous technology transfer seminars. The TSC will provide a very effective means for transferring the results of this research to the user community. The Air Force Environmental Systems Program Office (HSC/YAO) and the Air Force Center for Engineering Excellence (AFCEE/ES) will further develop the technical information and finalization of the technical data package. Preliminary principals of practice manuals, technical reports and professional publications will be produced for distribution to appropriate technology transfer offices of the Air Force, Army, Navy, and DOE.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	500	2200	2600	2800	1400	9500
EPA	530	678	700	750	400	3058
DoD*	629	462	138	0	0	1229
Total	1659	3340	3438	3550	1800	13787

* Armstrong Laboratory, Environics Directorate

12. Performers:

The performers for the proposed work are: EPA - Robert S. Kerr Environmental Research Laboratory, Ada, OK; University of Florida, Gainesville, FL; DoD (Air Force) - Armstrong Laboratory, Environics Directorate, Tyndall Air Force Base, FL; DoD (Air Force) - Environmental Management Directorate, Hill AFB, UT. Cooperative agreements with academic and research organizations already involved in development of aquifer remediation technology will be used to conduct part of the proposed research. CRADAs will be developed as the project progresses.

13. Principal Investigator:

Carl G. Enfield, Senior Research Environmental Scientist
US EPA, Robert S. Kerr Environmental Research Laboratory
P. O. Box 1198, Ada, Oklahoma 74820
Phone: (405) 436-8530
Fax: (405) 436-8582

14. Keywords:

extraction, NAPL, ground-water, surfactant, co-solvent, sparging

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Removal and Encapsulation of Heavy Metals from Ground Water

3. **Agency:** USEPA

4. **Laboratory:** Risk Reduction Engineering Laboratory

5. **Proposal ID:** #387

6. **Problem Statement:**

The goals of this proposed applied research (6.2) program are to develop a unique, innovative technological approach for many of the difficult problems, found on both DoD and DOE facilities: 1) that of removing metal contamination from dilute matrix (i.e water): 2) managing metal residuals that can not be destroyed: 3) protecting surplus equipment from environmental exposure. This effort will (1) develop high-capacity low-cost adsorbents, based on cellulose or starch, natural polymer or synthetic polymers (with functional groups) for selectively adsorbing toxic metals such as uranium, plutonium, mercury, and then (2) demonstrate permanent encapsulation of the solid adsorbent matrix by extrusion in recycled plastics such as high density polyethylene for long-term disposal, or (3) allow for temporary storage of these metals for future resource recovery or protection of surplus equipment from environmental exposure. The metal contaminants (i.e. mercury, lead, uranium) can be directly adsorbed from ground water or wastewater. If present in a solid matrix, the metals can first be leached selectively into a concentrated aqueous medium, which then will be subjected to the low-cost adsorption technique and encapsulation. Likewise, this encapsulation concept has application to solid material such as depleted uranium or plutonium found at the Y12 plant, Rocky Flats, or Aberdeen Proving Ground. The proposed research will result in a highly efficient, yet affordable technology for remediating metal contaminated water as well as protect surplus equipment from environmental exposure.

Restoration of metal-contaminated water or solids is a generic problem, with many sites belonging to both DOE and DoD. Indeed the problem is so extensive that affordable technologies are critically needed now. For ground water the dominant methods used today are of the pump-and-treat type. The treatment part usually uses activated carbon or a resin, which on saturation is regenerated by acid leaching. The metals in aqueous stream are then isolated by precipitation. The precipitate sludge is further treated, then disposed of in a hazardous waste landfill. The problem may continue over the years as the metals will gradually form leachates. It has been estimated by industry that for every one dollar of operating cost in the adsorption part of this technology, about 3 to 6 dollars are spent in regeneration. Thus developing low-cost adsorbents that do not need regeneration provides a very attractive technical approach. This is a new idea, no prior art exists.

One dominant method of metals disposal is the cement-based solidification/stabilization process. The long-term effectiveness of this technique, however, has not been determined. Alternatively vitrification has been tried, and proposed especially for radioactive wastes but does not allow for resource recovery of the encapsulated material. Encapsulating radioactive wastes in thermoplastics has been demonstrated in the U.S., U.K., France, and Israel, and no leaching has

been observed for a long time (years). Metals and their compounds have no detectable diffusive transport through polymer films. In landfills thermoplastics do not begin to biodegrade in less than 400 years; in low moisture environment and in absence of microbial action, therefore, these encapsulants will last much longer. The thermoplastics are also stable to high levels of irradiation, which is important for storing radioactive compounds. The longevity of these encapsulants of course can be increased by multiple encapsulation. The Brookhaven National laboratory and the University of Cincinnati have done some preliminary work in this area. Furthermore, temporary encapsulation of surplus DoD material will alleviate many of the concerns expressed in the Office of Technology Assessment's critical report of DoD's equipment storage systems that are wasting millions of dollars due to corrosion from unprotected environmental exposure.

This is a project program that has never been funded before.

7. Project Description:

The project has several distinct parts, requiring different technical skills for their solution. First, low-cost adsorbents need to be designed and developed and produced. In the environmental restoration area, adsorbents such as carbon, zeolites, or ion exchange resins have been used. Each technology is based on the concept of regenerating the adsorbents for reuse. As has been mentioned before, even with regeneration, these adsorption processes tend to be very expensive for large dilute matrices. Moreover these adsorbents do not possess high adsorption capacity (mostly fraction of a percent), which imparts two undesirable effects on process economics, namely adsorbent cost and eventual dilution of the metals on regeneration. Highly selective adsorbents with specific ligands have made chromatography a mainstay in protein separation from very dilute solutions. In that spirit, this effort will develop low-cost adsorbents which have inexpensive but highly efficient ligands attached to them. These adsorbents will have higher capacity and high specificity for chosen metals. The resulting adsorbents will not need to be regenerated.

The technical approach consists of attaching specific amine or imine-based (or other promising) ligands on chosen adsorbents, which can be selected from cellulose, starch, saw dust, peat moss, chitin/chitosan etc., and tested for their efficacy. EPA has discussed the prospect of this approach with Prof. Jerker Porath, the famous inventor of sepharose and sephadex, the two universally used chromatography column material. Prof. Porath, who spends six months at Upsala University in Sweden and the rest at the University of Arizona, is interested in collaboration with EPA. Prof. Porath will take the prime responsibility of synthesizing the low-cost adsorbents. The engineered material most likely will be in pellets or beads form. EPA will build laboratory apparatus to demonstrate the idea of metals adsorption from contaminated water. For uranium, or plutonium, a toxic metal surrogate will be used.

In another section of the project, the separation (volume reduction) data from the laboratory will be used to design experiments for encapsulating the adsorbents or for encapsulating surplus equipment in recyclable plastics, to reduce life cycle cost. Prof. Don White, a plastics conversion specialist, and Prof. David Wolf (working at the University of Arizona) would be responsible for this effort. EPA will have access to the University extruders for demonstrating the technology. Lastly, EPA will propose demonstrating this concept at a DoD or DOE site.

Important technical issues to overcome: (i) attaching inexpensive ligands to low-cost substrate to impart high capacity, (ii) preparing appropriate engineered (thermoplastic) materials which

are easily handled, (iii) demonstrating the stability of the polymers to internal or environmental effects such as radiation and (iv) demonstrating ability of resource recovery of both the encapsulated heavy metals and thermoplastic material.

8. Expected Payoff:

This technological approach can be tailor-made to many civilian or military site-related problems. This approach will establish a new paradigm in adsorption technology -- i.e. disposal with adsorption without regeneration.

Impact: This technology will have far-reaching impact on particularly dilute contaminated matrices for which no inexpensive alternatives exist. In addition, this technology will allow resource recovery, when needed, from solid material such as uranium. Also, millions of dollars of DoD equipment can be protected from environment exposure. Life cycle cost can be reduced if the encapsulating material is recyclable.

9. Milestones:

Assume funding initiated in 09/94:

1. Low-cost adsorbents developed and tested in the laboratory. Encapsulation work without metal loading begun. 09/95

2. Laboratory work completed to provide design data for encapsulation. Encapsulation demonstration using extrusion completed. 09/96

3. Final Product: Process specification provided for demonstration at a DoD or DOE site. 09/97

10. Transition Plan:

After 24 months technical support will be provided to build prototype for demonstration of technology at a DoD or DOE site.

11. Funding: ($K)

EPA has already allocated $100K towards basic research into low-cost adsorbents research. WES has spent this much on starch xanthates.

	FY94	FY95	FY96	TOTAL
SERDP	350	350	400	1100

12. Performers:

EPA Risk Reduction Engineering Laboratory (Sikdar, Barth); Cooperative research agreement with University of Arizona; and University of Cincinnati; Waterways Experimental Station Mark Bricka, PhD., Waterways Experimental Station, 601-634-3700, Fax 601-634-3833

Brookhaven National Laboratory (Colombo, Kalb)
Peter Colombo, Head, Environmental and Waste Technology Center, BNL
516-282-7644, Fax 516-282-5305;
Paul Kalb, Group Leader, Waste Treatment and Disposal, BNL,
516-282-7644, Fax 516-282-5305

13. Principal Investigators:

Subhas K. Sikdar, Ph.D., Director
Water & Hazardous Waste Treatment Research Division, RREL
Edwin Barth; P.E.
Environmental Engineer
Center for Environmental Research Information
Risk Reduction Engineering Laboratory
Cincinnati, OH
Tel: 513 569-7528 Fax: 513 569-7787 (Sikdar)
Tel: 513 569-7669 Fax: 513 569 7585 (Barth)

Sponsoring Organizations:

Jeffrey S. Walker
Program Manager
Office of Technology Demonstration
U.S. DOE
EM 542 Trevion II
1000 Independence Ave, SW
Washington, DC 20585
Phone: 301 903-7966
Fax: 301 903-7457

Robert Scola
Director, Environmental R&D
Army Production Base
Modernization Activity
Bldg. 172 AMSMC-PB
Picatinny Arsenal
Dover, NJ 07806
Phone: 201 724-2044
Fax: 201 724-4407

14. Keywords:

Adsorbents, Encapsulation, Recycled Plastics, Ligands, Metal-binding

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Encapsulated Bacteria for In Situ PAH Bioremediation

3. **Agency:** Navy

4. **Laboratory:** NRL

5. **Proposal ID:** #023

6. **Problem Statement:**

This proposal addresses Requirement 1.I.4.m, and is for the continuation of an existing SERDP-funded project entitled 'Encapsulated or Immobilized Enzymes, Bacteria and Nutrients for Remediation of Fuel Spills' and is applied research (6.2/6.3).

The soils and sediments at Naval refueling facilities are often contaminated with petroleum products that are classified as hazardous wastes. The petroleum products that remain as long term contaminants, include polycyclic aromatic hydrocarbons (PAHs; hazardous waste CFR# K001). Removal and cleanup of these materials is expensive and disruptive to Naval operations. Current methods for treatment of contaminated harbor sediments involve dredging with subsequent off-site detoxification. Development of remediation technologies that treat contaminated soils and sediments in situ, would save the Navy considerable expense and eliminate procedures disruptive to Naval operations.

This project addresses the SERDP goals of lowering environmental cleanup costs, compliance with environmental regulations, and unencumbrance of military operations. It focuses on the Thrust Area of cleanup of soil, sediment, groundwater, and subsurface water. The overall goal of this project is to develop an in situ treatment strategy using microencapsulated bacteria for low-cost bioremediation of petroleum products that are poorly degraded by naturally-occurring bacteria. In situ treatment strategies lower the cost over ex situ treatments by eliminating the need for expensive excavation, transportation, and storage of the hazardous waste prior to detoxification.

If successful, this treatment strategy may be useful for remediation of some toxic hot spots (PAH contamination) in San Diego Bay sediments. The magnitude of the problem, in terms of PAH contamination, is considerable as the sediment of nearly every harbor is contaminated from ship oil and creosote treatment of docks. In San Diego Harbor alone, nearly 4.5 million cubic yards of sediment is being dredged for Naval harbor deepening projects (e.g. carrier turnaround basin, Pier Bravo), with an expected 0.5 million cubic yards being too contaminated for oceanic dumping or beach replenishment projects. According to the San Diego Regional Quality Control Board, once sites in the Bay are declared 'toxic hot spots', dredging and off-site disposal will not be a legal means of detoxification as a precursor to harbor deepening. In lieu of effective in situ remediation technologies, such as this microencapsulated bacteria strategy, the Navy will either have to receive an exemption from the law (which may lead to public relations difficulties) or will have to limit access of Naval vessels to the base. These harbor and pier deepening projects should be considered crucial for continued Naval vessel access to the base. Even if this proposed strategy is not successful at complete removal of the toxicant, treatment may lower

PAH levels to the threshold that would allow for the dredging and further off-site cleanup of the sediment.

7. Project Description:

With previous SERDP funding, strains of petroleum-degrading bacteria were microencapsulated in an alginate matrix cross-linked with divalent cation bridges (calcium). The published system has been adapted using an internal set with solid calcium particles. As the calcium slowly solubilizes in the alginate matrix, the cross-links form which encapsulate the bacteria. This adaptation is expected to reduce ionic stress to the bacteria, resulting in increased encapsulation efficiencies and higher cell viability with long term storage. Higher encapsulation efficiencies and cell viability lowers the cost of the bioremediation treatment strategy.

For the bacterial microencapsulation strategy to be successful and low-cost, the conditions for encapsulation have been optimized to enhance cell viability and petroleum-degrading activity. By developing such a system, fewer microcapsules are needed per volume of treated material, thus lowering the overall treatment cost. Bacterial growth conditions prior to encapsulation have been examined for their effect on cell viability. In addition, the effect of various storage conditions (lyophilization, refrigeration, freezing) on cell viability of encapsulated bacteria was determined to enhance treatment effectiveness. These tasks address the primary environmental concern of ensuring the use of effective and affordable remediation technology.

Microencapsulation of petroleum-degrading bacteria allows for the storage and delivery of strains that are normally found in nature, but may be present in reduced abundance at the spill site. These strains were originally isolated from Superfund sites that were contaminated over decades with creosote. Over time, similar strains will increase in abundance at the spill sites resulting in eventual degradation of the petroleum, but this process may take fifty years or more. The goal is to use microencapsulated bacteria to reduce the contamination level over time scales of months instead of decades. This would reduce exposure of Naval personnel to toxic and carcinogenic waste, and enable the site to be used by either the Navy or the public sector within a reasonable time frame and at an acceptable cost.

Poor performance of in situ treatments involving the addition of bacteria have been due to the unknown effects of site conditions on the ability of bacteria to degrade contaminants. NRL is currently developing specialized indicator strains of bacteria that produce light in response to the presence of bioavailable PAH. The indicator strains would enable us to predetermine, whether or not the appropriate nutrient and environmental conditions exist at a site making it amenable to the in situ treatment using microencapsulated bacteria. This system would allow us to alter the site conditions, with nutrients or buffers, prior to adding the bacteria. Though this project involves the construction of genetically engineered strains for assays, it does not involve the release of genetically engineered bacteria into the environment.

Previously, it has been demonstrated that disturbing contaminated soils has resulted in abiotic removal of the toxin from the site. These treatments have often erroneously been characterized as 'bioremediation'. To determine whether or not the microencapsulation treatment is resulting in actual bacterial degradation of PAH at the site, newly developed molecular probing techniques (16S rRNA hybridization) will be used to identify the added PAH-degrading bacteria in the soils and sediments. These tasks address the primary environmental concern to implement affordable methods for site characterization, namely the field location and abundance of PAH-degrading bacteria.

The microencapsulated bacteria will be tested as a bioremediation strategy in model microcosm systems (5 liter) and subsequently in pilot-plant scale systems (100 liter). These series of tests will be designed to demonstrate the potential of employing microencapsulated PAH-degrading bacteria, along with essential inorganic nutrients and electron acceptors, as part of an in situ bioremediation strategy. Finally, the system will be field tested in coordination with an EPA project examining the use of stable isotopic methods for determining efficacy of bioremediation treatments. This important collaboration will help determine the effectiveness of microencapsulated bacteria at degrading PAH under field conditions.

8. Expected Payoff:

Using microencapsulated bacteria to detoxify a site of hazardous waste compounds would be a low-cost alternative to excavation and off-site treatment of contaminated soils. Aside from the lower cost of removal of PAH from Naval soils and sediments, an important aspect of the strategy is that Naval operations in the treated area are less disrupted when compared with treatment requiring excavation and off-site cleanup. It is exceedingly difficult to estimates of the dollar value of this savings to the Navy. Also, because of the potential of causing collateral damage to areas adjacent to the treated area, there is sometimes no alternate ex situ treatment that can be used for cost comparison. In situations where soils and sediments are co-contaminated with heavy metals and PAH, removal of PAH allows for the immobilization of the metals with subsequent landfilling of the treated materials.

9. Milestones:

1.	Complete review of technologies. Completed	9/92
2.	Define and optimize microencapsulation procedures. Completed	5/93
3.	Coencapsulate nutrients. Completed	7/93
4.	Encapsulate densifying agents. Completed	8/93
5.	Optimize encapsulation for enhanced bacterial viability. Completed	11/93
6.	Completed development of microcapsule system. Completed	11/93
7.	Construct microcosm model testing system.	11/93
8.	Perform benchtop assays of petroleum degradation.	3/94
9.	Scale up of 8. (microcosm model system)	6/94
10.	Complete development of indicator strain assay.	6/94
11.	Evaluate molecular probe techniques for treatment efficacy in microcosm model.	7/94
12.	Test treatment in second microcosm evaluation.	10/94
13.	Treatment efficacy in model system.	3/95
14.	Optimize treatment for test site field conditions.	5/95
15.	Physical characterization of test site.	7/95
16.	Field demonstration of treatment system.	8/95
17.	Final report.	9/96

10. Transition Plan:

The technology will be transitioned to the industrial collaborator, SBP Technologies, Inc. SBP and its parent company, Eicon, have the technology base and expertise and equipment necessary to use this treatment strategy for eventual cleanup of Naval sites. Their research facilities are on-site at the EPA's Gulf Breeze Environmental Research Lab in Pensacola, FL where they work on encapsulated and immobilized cell technologies for creosote degradation in bioreactors.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP/NRL	180	250	350	350	350	1480
SBP	0	50	150	50	200	450
TOTAL						1930

12. Performers:

The lead organization is NRL Code 6900 (Center for Biomolecular Science and Engineering). The principal contractor is SBP Technologies, Inc. (POC: Dr. James Mueller). Development of methods for determining treatment efficacy is being coordinated with management of a SERDP funded project at EPA (POC: Dr. Raymond Wilhour, Gulf Breeze Environmental Research Lab, Pensacola, FL).

NRL: Dr. Bruce Gaber, Program Manager, Dr. Michael Montgomery, Environmental Microbiology, Mr. David Flaherty, Molecular Genetics

Collaboration with Industry, SBP, Technologies, Inc., Dr. James Mueller, PAH Bioremediation Ms. Susanne Lantz, Bioremediation.

Collaboration with EPA's Gulf Breeze Environmental Research Lab, Dr. Hap Pritchard, Branch Chief, Bioremediation and Risk Assessment, Dr. Richard Coffin, Microbial Ecology Group Head

13. Principal Investigator:

Dr. Bruce Gaber
NRL Code 6900
4555 Overlook Avenue
Washington, DC 20375
TEL: (202) 767-3344
FAX: (202) 767-1295

14. Keywords:

Bioremediation; petroleum; PAH; bacteria; in situ.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** In Situ Bioremediation of Fuel and Efficacy Monitoring.

3. **Agency:** Navy

4. **Laboratory:** NRL

5. **Proposal ID:** #030

6. **Problem Statement:**

This proposal (6.2/6.3) addresses Requirement 1.III.1.g & j. Contamination of soil, sediment and waters by fossil fuel-based contaminants represents the world's largest environmental problem. In the U.S., the frequency of occurrence of fossil fuel contamination is greater in magnitude than that reported for chlorinated solvent pollution. Given the scope and magnitude of these environmental contamination problems, bioremediation often represents the only practical and economically feasible solution. When depth of contamination or nature of contaminated material precludes all other remedial actions short of the no-response alternative, in situ treatments are frequently recommended. However, cost-efficient and effective implementation strategies need to be specifically developed and/or refined to address these needs. At the same time, unequivocal approaches for demonstrating in situ bioremediation of target contaminants need to be established.

With past support of the SERDP program we have developed and refined innovative in situ bioremediation strategies including approaches using stable carbon and nitrogen isotope geochemistry to monitor progress during in situ bioremediation of polycyclic aromatic hydrocarbons (PAHs) and other priority pollutants (e.g., BTEX). Approaches in stable isotope geochemistry may allow one to monitor progress of the bioremediation effort by tracing the fate of individual compounds of interest: including bacterial assimilation and respiration, formation of toxic intermediates, and transport of the compound from the site. With this information, a mass balance for a contaminant may be conducted and efficacy of various bioremediation approaches may be tested.

To establish tests using stable isotopes as a monitoring protocol for bioremediation, SERDP has funded researchers at Gulf Breeze Environmental Research Laboratory (GBERL), Texas A&M University (TAMU), Naval Research Laboratory (NRL) and SBP Technologies, Inc. (SBP) to setup stable isotope laboratories and to conduct preliminary experiments. The objective of the current proposal is to transition this 6.2/6.3 research, through a series of field demonstration programs, yielding valid, cost-efficient technologies for in situ bioremediation and on-line performance monitoring. A coordination plan, not included herein, with CU-720 (Integrated Biotreatment Research Program-Army), CU-428 (Ground Water Cleanup) and CU-723 (National Environmental Test Site Program). Sites included in CU-723 will be included in the project.

This is a continuation of an on-line project.

7. Project Description:

Collaborating researchers at the GBERL, NRL, SBP, and TAMU received SERDP funds in June of 1993. The progress of these collaborations to date is as follows. Two laboratories have been equipped with elemental analyzer/ gas chromatograph/ isotope ratio mass spectrometers (EA/GC/IRMS). One system at TAMU is dedicated to measuring natural abundance stable isotope ratios. The other system at GBERL is set up for experiments with tracer additions of stable isotopes. Each is equipped so that carbon, nitrogen and sulfur isotope ratios may be measured as gases, gross organic matter or as individual compounds. One is also equipped with an ion trap mass spectrometer (ITMS) to assist with compound identification. This addition will make it possible to follow intermediate compounds during the degradation process.

The development of methods to measure bioremediation effectiveness involved the in situ degradation of PAH mixtures in lab systems. Drs. Cifuentes and Coffin have been measuring the natural abundance carbon isotope ratio of CO_2 that is evolved upon degradation of various mixtures of compounds. Results indicate a direct correspondence of the stable carbon isotope ratio of CO_2 and the carbon source that is respired by bacteria. This information suggests that on-line monitoring of CO_2 carbon isotope ratios will be appropriate for examining, monitoring and evaluating the bioremediation of contaminant mixtures.

Along with the development of stable isotope monitoring tools, SBP has integrated innovative technologies and support from various other industrial collaborators (i.e., Beazer East, Inc., Chevron, IEG Technologies, Inc.) to yield full-scale and practical applications for in situ bioremediation strategies. Various modifications of in situ soil flushing, aeration, and groundwater circulation technologies have proven effective for simultaneous treatment of vadose/phreatic zone soil, capillary fringe, groundwater and saturated soil contaminated with refined petroleum products at over 100 sites world-wide. However, successful application to environments contaminated with more biologically persistent compounds, such as jet fuel constituents and certain PAHs, has been somewhat limited. Presently, there are few examples of successful in situ bioremediation projects in the technological database. Moreover, trial demonstrations of more conventional bioremediation approaches, such as hydrogen peroxide injection and pump-and-treat technologies, have met with limited success in their applications to PAH contaminated environments. Two key factors responsible for this poor performance are bioavailability and presence of PAH-degrading microorganisms.

The program objective is to demonstrate the usefulness of innovative in situ bioremediation technologies by introducing inoculants and maintaining their activity in the field. The project approach is to develop the treatment strategy, identify the contaminated site, employ the biotreatment in small-scale laboratory tests, and finally in a large-scale field demonstration. This project has three unique thrust areas: development of techniques for measuring effectiveness of bioremediation treatments; integration of multiple technologies for treatment strategy; and, use of bacterial encapsulation and inoculation for enhancement of PAH degradation in the field. Laboratory studies will model the biodegradation of individual chemicals by axenic bacterial cultures available in our culture collections. The studies will be used to measure biodegradation rates, identify catabolic intermediates, assess the formation of toxic end-products, and perform mass balances of the contaminant under controlled and defined conditions. Similar studies will be conducted with field samples to define the fate and effect of parent compounds and biotransformation products for mass balances.

Activity and survival of microencapsulated PAH-degrading bacteria will be characterized. For example, new, more efficient strains may be encapsulated and applications for different environments will be considered. Researchers at NRL will examine a series of microbially produced biosurfactants for use in the enhancement of degradation of PAHs bound to soil and sediment surfaces. The optimal conditions for production of biosurfactants in field systems will also be determined. Successful completion of this task would expand the use of the well treatment system to include PAH remediation in soils. Under a separate task, NRL will continue to lead the development of indicator strains of bacteria that will enable us to better monitor successful bioremediation attributable to the introduction of encapsulated microorganisms.

Samples of contaminated soil will be thoroughly characterized according to standard methods. Contaminants will be extracted, fractionated and chemically analyzed: the natural abundance isotope ratios of these materials will be determined. These values will be compared with those for indigenous carbon sources (i.e., humic materials, humin, fulvic acid, et cetera). Knowing these values, mineralization of contaminants will be assessed by the $^{12}C/^{13}C$ ratio of liberated CO_2. These values will be compared with those generated using more conventional chemical and biological analyses. The effect of various amendments on contaminant degradation by naturally-occurring bacteria will be determined.

Mesocosms will be constructed to conduct studies examining the ability of in situ soil flushing and groundwater circulation well (GCW) technology, combined with subsurface bioreactors employing co-immobilized biodegradation agents to biodegrade PAHs. The mesocosms will be loaded with aquifer material artificially contaminated with a known amount of pollutant. The system will be monitored using on-line measurements of microbial respiration, water movement, etc. Stable isotope analyses will help monitor environmental fate of transformed chemicals. This test system will allow for mass balance chemical analyses to document biodegradation of target compounds using these stable isotope techniques. As recommended by the SERDP Science Advisory Board (SAB), field-scale demonstrations will be conducted at five or more contaminated sites to test the efficacy of the monitoring technology across five different remediation strategies. Sites will be offered through collaboration with Chevron (refined petroleum products), Beazer East, Inc. (creosote), and the Navy (jet fuel). Sites will be characterized and the bioremediation process will be monitored for 2 years. Field work will be conducted to use natural abundance stable carbon isotope ratios of CO_2 to measure the degradation of PAH mixtures. This work will involve surveys of natural abundance isotope ratios of pollutant compounds, extracted mixtures of pollutants, indigenous/natural organic matter, PAHs and CO_2 evolving from field sites. "CO_2 collection chambers" will collect gases from soil or groundwater wells thus providing on-line, real-time analysis of bioremediation performance.

8. Expected Payoff:

Techniques for assessing efficacy of remedial technologies are critically needed. Such tools are essential to help ensure that the efforts undertaken are effective and that the remedial technologies are implemented in a cost-efficient manner. Using conventional chemical and biological assays in combination with the proposed on-line stable isotope analyses developed here, offers an ability to follow assimilation, respiration, immobilization, transport and biotransformation of pollutants in situ. The payoff is development of the first unequivocal assessment of treatment efficacy for in situ bioremediation strategies.

9. Milestones:

1.	Report on laboratory studies of biodegradation using stable isotope analyses.	12/94
2.	Initiate field studies via site characterization, system installation, and generation of data.	3/95
3.	Report on mesocosm tests using GVW well technology and an in situ bioreactor.	8/95
4.	Report on the results of pilot-scale field demos.	8/96
5.	Final report on the results of pilot-scale field demos.	8/97

10. Transition Plan:

Rapid and successful transition of developed technology from demonstration stage to full-scale implementation is enhanced through the active participation of SBP Technologies, Inc. (an EICON Company) and other industrial affiliates (IEG Technologies, Inc.). EICON is a holding company for 85+ professionals employed by: 1) SBP (remedial services, technology development), 2) Environmental Laboratories, Inc. (site characterization, engineering, analytical testing and services), 3) FGA Services, Inc. (civil and public works engineering), 4) FGA Surveys, Inc. (land surveying capabilities, engineering), 5) Ver-Val Environmental Enterprises, Inc. (mechanical engineering, fabrication, and general environmental services); and 6) Westcott & Mapes, Inc. (architectural and engineering services). EICON has over 20 years of experience in environmental services and engineering. With a number of dedicated end-users (i.e., Beazer East, Inc., Chevron) active in this and previous stages of technology development, we are convinced that we have integrated expertise in all aspects of technology development, commercialization and full-scale implementation of systems.

11. Funding: ($K)

Group	Description	Phase I	FY94	FY95	FY96
NRL	biosurfactants	0	350	200	150
GBERL	Monitoring Technology	500	400	150	150
TAMU	stable isotope measurements	200	200	150	150
SBP	field demos/ characterize site	0	1500	250	250
Total		700	2450	750	700

12. Performers:

NRL, EPA GBERL, TAMU, SBP

13. Principal Investigator:

Capt. Warren Schultz
Naval Research Laboratory
Code 6106
4555 Overlook Avenue
Washington, DC, 20375-5348
TEL: 202-767-0192
FAX: 202-404-7139

14. Keywords:

Cleanup, bioremediation, fuels, bacteria, in situ.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Air Sparging and In-Situ Bioremediation Research and Demonstration

3. **Agency:** Army

4. **Laboratory:** Picatinny Arsenal, New Jersey

5. **Proposal ID:** #744

6. **Problem Statement:**

Goal: Bioremediation enhancement to air sparging technology may provide a cost effective strategy for removing trichlorethylene (TCE) and related chlorinated solvents from ground water. However, unresolved technical issues focus on quantifying the incremental benefit and designing efforts to stimulate microbial degradation. The overall goal of Phase I of this project is to develop laboratory and field methods for determining the effect of sparge gas-composition on the partition of mass removal due to volatilization and microbial processes. The methods will be demonstrated at Picatinny Arsenal, New Jersey, a site with a well-characterized plume of TCE contamination. Phase II of the project will involve the design and operation of a full-scale sparging/bioremediation demonstration at Picatinny Arsenal based on the findings of Phase I. The overall project will resolve technical and institutional issues that inhibit operational use of the technology.

Background: Air-sparging and coupled in-situ bioremediation has been implemented at the Savannah River site. The Savannah River Project was designed as a scientific demonstration. In addition, the site is characterized by specific geochemical conditions, most notably, the plume was aerobic. An anaerobic contaminant plume, like the one at Picatinny Arsenal, is perhaps more typical of TCE plumes, and introduces questions related to the rate of adaption of the microbial consortium and engineering considerations related to induced precipitates.

TCE is the dominant contaminant in a plume within an unconfined glacial aquifer at Picatinny Arsenal. The unconfined aquifer is about 50 feet thick in the vicinity of the contaminant plume. In 1991, the highest measured concentration of TCE was 21,000 micrograms per liter. In 1986, the site was selected by the USGS Toxic Substances Hydrology Program as its research site chlorinated solvents. Research includes characterization of TCE, related contaminants, and contaminant geochemistry in the aquifer and the unsaturated zone, and fate and transport evaluation. The army has initiated an interim action under CERCLA to contain and treat the plume by pumping before it enters a continuing source of contamination may necessitate that the pump and treat operation continue indefinitely. The enhanced sparging technology could mitigate this condition.

7. Project Description:

Technical Objective: The objective is to develop methods to quantify the total rate of removal of TCE contaminant for an air sparging remediation system adapted to enhance contaminant removal with aerobic cometabolism. The total rate of removal is the sum of a component due to physical stripping (volatilization) and a component due to aerobic cometabolism. Both components will be quantified to allow for an evaluation of the cost effectiveness of the microbial enhancement. The methods are to be demonstrated at an existing site of TCE contamination and in the laboratory with porous media collected from the site.

Technical Approach: The workplan has three major components: (1) development of methods to conduct sparging/cometabolism laboratory experiments with contaminated sediment, (2) application of overall method to pilot scale experiments at Picatinny Arsenal, and (3) development of a mathematical model to analyze the transport of sparged vapor phase constituents from the water table to extraction wells for the purpose of determining the distribution of mass flux across the water table.

Site geochemistry will be monitored to assess initial conditions with respect to a wide range of inorganic and organic solutes. Initial site assessment will also include analysis of sediment cores to define lithology, total contaminant mass, physical characteristics, and selected microbial guild characterizations.

Laboratory experiments will be conducted with sediment collected during the site assessment described above. Two types of experiments will be conducted: closed systems microcosm experiments and open system column experiments. The microcosm experiments will determine the feasibility of aerobic cometabolism over the range of anticipated geochemical conditions and methane concentration. The open column experiments will allow for emulation of the field experiments under controlled conditions. Cores of sediment taken from the Picatinny site will be instrumented for the columns. Control experiments conducted with pure nitrogen as the sparge gas will provide physical removal rate information to be compared with experiments conducted with sparge gases with various methane and oxygen concentration. These experiments will allow for quantification of the effect of varying design parameters on system performance. The information obtained for the Picatinny sediment will allow for the rational design of pilot-scale experiments.

Pilot scale sparging experiments will be conducted at Picatinny Arsenal within the well-characterized site. The purpose of these experiments is to apply the overall method insitu and to demonstrate the scaling up of laboratory information and application of the mathematical model (discussed below). The experiments will be conducted with a single sparge well. Mass removal rates will be calculated by collecting vapors with a vapor extraction well and analyzing the exhaust stream for a wide suite of vapors, including TCE and related contaminants, methane as well as signature gasses like carbon dioxide, oxygen, and hydrogen sulfide. The monitoring will allow for separation of removal into a physical volatilization component and into a microbial component inferred by stoichiometric relationship to signature gases. It is anticipated that the experiment can be repeated at the same location to study variable injection rates and methane loading after a time interval passes which allows for the recontamination of the sparged column from surrounding ground water. It is anticipated that pilot scale experiments can be by-passed in subsequent operational applications of the technology.

A mathematical model of the vapor extraction process will be constructed to determine the spatial effect of the sparge well by allowing for the calculation of constituent-specific mass flux across the water table to the extraction well. Reactions that occur in the unsaturated zone while TCE, methane and oxygen are in transit to the extraction well(s) will also be simulated. This model is currently under development at U.S.G.S. It will be completed, applied, and published as a public domain code during this project.

8. Expected Payoffs:

(1) Development of methods for performance evaluation and development of design criteria for air sparging with bioremediation enhancement.

(2) Demonstration of methods at a site with geochemical conditions different than previously investigated at Savannah River.

9. Milestones:

Progress To Date (11/12/93): This proposal was approved for first year funding during the fiscal year 1993. SERDP selection process funding outlays have been planned at this time but as yet funds have not been awarded to the participants. An expert advisory panel has been contacted and organized. The members, listed in a previous section, provide technical oversight and guidance in a broad range of disciplines. The USGS research staff has been assembled and includes Dr. Arthur Baehr, Mr. Jeffrey Fisher, Dr. Timothy P. Wilson, and Dr. Ronald J. Baker. Contact has been made with Dr. Clifford Bruell, Department of Civil Engineering, University of Mass. at Lowell, to cooperate in the design and execution of column experiments to analyze processes related to air sparging. A laboratory has been established at the Picatinny Arsenal field site. The laboratory is equipped fully to analyze for volatile organic compounds in water or vapor samples collected at the field site.

10. Transition Plan:

The subject technology, which was develop under a DOE program, will be implemented at a DoD site under regulatory auspices of the U.S. Environmental Protection Agency and the New Jersey Dept. of Env. Protection and Energy. Appropriate aspects of the project will be published in peer review journals.

11. Funding:

Schedule Phase I:

	1994 Year 1	1995 Year 2	1996 Year 3
USGS	502	453	163
U.S. Army Contractor	40	20	10
HSMRC	15	25	15
Total	557	498	188

12. Performers:

U.S. Army- Coordinate contractor procurement and regulatory compliance

U.S. Geological Survey- responsible for conducting Phase I research

Private Contractor- assist in the design of vapor extraction system and development of unsaturated zone transport model in cooperation with U.S.G.S.

Hazardous Substance Management Research Center (HSMRC)- coordinate and chair expert advisory panel which will provide technical oversight

Expert Advisory Panel:

Dr. Richard Brown: Groundwater Technologies Inc., Princeton, N.J., Dr. Peter Jaffe: Dept. of Civil Engineering, Princeton University, Dr. Peter Lederman: Director, Center for Environmental Engineering and Science, N.J. Institute of Technology:; Dr. Brian Looney: Westinghouse Savannah River, Aiken, S.C.; Dr. John Wilson: USEPA, Kerr Research Lab, Ada, Oklahoma

13. Principal Investigators:

Mr. Herbert Buxton
U.S. Geological Survey
810 Bear Tavern Road
West Trenton, N.J. 08628
TEL: (609) 771-3900
FAX: (609) 771-3915

Mr Thomas Solecki
ARDEC, ATTN: SMCAR-SEA, Bldg. 1
Picatinny Arsenal, N.J. 07806-6582
TEL: (201) 724-5818
FAX: (201) 724-6582

14. Keywords:

Air sparging, TCE, chlorinated solvents, bioremediation enhancement, ground water remediation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Explosives Conjugation Products in Remediation Matrices

3. **Agency:** Army Corps of Engineers

4. **Laboratory:** Waterways Experiment Station (WES)

5. **Proposal ID:** #715

6. **Problem Statement:**

During investigations of potential treatment technologies for explosives contaminated soils, specifically during bioslurry treatability studies and composting, TNT has been observed to interact with some component of the treatment matrix in such a way as to preclude extraction with organic solvents. Similar interactions have been observed in explosives amended soils. Mass balance determinations using radiolabelled TNT reveal that the radioactivity is still present in the matrix in some unknown form. As much as 80 percent of the radioactivity added to tests is accounted for in the unextractable matrix. Therefore, the parent compound has not been completely destroyed, but has changed to a more complex form. The long-term stability and environmental safety of these uncharacterized conjugates are unknown. Objectives of this basic research include characterization of these explosives conjugates, development of an analytical methods for identifying them in treatment systems and in soils, and determining the long-term stability and environmental safety of the conjugates. Accomplishment of these objectives will ensure the development of effective remediation technologies that ameliorate environmental health effects and lead to a more complete characterization of the end products of new treatment technologies. Research was initiated to determine the basic mechanisms of interactions between TNT and humus, soil enzymes and clays under SERDP in FY 93. This proposed research would expand upon that effort.

7. **Project Description:**

The project will consist of five tasks as follow:

Task 1: Characterization of interactions of explosives with humus and other organic components of soils and remediation matrices.
Task 2: Characterization of interactions of explosives with clays and other mineral components of soils and remediation matrices.
Task 3: Development of an analytical method for identifying conjugates in various matrices.
Task 4: Determination of the role of microbiological processes in formation and stability of conjugates.
Task 5: Assessment of the ecotoxicology of conjugates.

The ability of explosives to form conjugates with soil organic fractions (i.e., humin, humic acids, fulvic acids, and enzymes such as peroxidase, laccase, and tyrosinase), clays (i.e., montmorillonites and kaolinites), and other mineral components of remediation matrices (i.e., oxy/hydroxy compounds of iron and other minerals) will be evaluated. The influence of environmental factors such as temperature, Ph and moisture regimes on development and

characteristics of conjugates will also be determined. Classical extraction and analytical techniques have been ineffective in removing and describing these unextractable conjugates. Therefore, innovative analytical techniques such as surface plasmon resonance, microcalorimetric titration, and new application of high performance liquid chromatography, X-ray diffraction and nuclear magnetic resonance will be applied. The role of microbial processes in the formation of the conjugates through precursor compounds or conjugation of explosive to microbial cell walls will be investigated. Factors affecting stability of the conjugates to leaching and microbial degradation will be determined.

Characterization of the ecotoxicology of conjugates answer the question of whether conjugates in soils and remediation matrices are environmentally compatible. An appropriate bioassay/biomarker suite will be selected based on the chemical nature of the parent compounds, the conjugates, and the potential functional groups present in metabolites. The potential for reappearance of toxicity from hydrolysis and re-release of parent compound or from the formation of toxic metabolites will be investigated. Microbial mutagenic and cultured cell line *in vitro* assays, and whole organism adult and early life-stage bioassays will be used. The influence of environmental factors on bioavailability and on the time course of toxic potency will be determined.

Specific user requirements that will benefit from performance of this work include:
(1.I.1.b) Technology for removal of energetics/other organics contamination (A,N)()(F)
(1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)()(F)

8. Expected Payoff:

This study will improve existing and future remediation technologies by identifying the composition and potential environmental impacts of explosives conjugates. The credibility of several existing technologies will be enhanced with regulatory agencies and with other users who are concerned with the ultimate safety and environmental effects of explosives. An understanding of the nature and properties of conjugation products formed during remediation and their fate and effects may also lead to new approaches to remediation.

9. Milestones:

1. Evaluate dialysis methods for assessing interaction with soil organic components (Natick)	03/94
2. Evaluate extraction and/or derivitization techniques for analytical methods development (CRREL)	07/94
3. Determine degradation rates for soil fractions containing explosives conjugates (WES)	09/94
4. Evaluate nuclear magnetic resonance techniques for determining interactions with clays (WES)	09/94
5. Select bioassay/biomarker toxicity tests for determining environmental safety of conjugates (WES)	03/94
6. Evaluate surface plasmon resonance for measuring binding kinetics of organic conjugates (Natick)	03/95
7. Develop extraction and analysis procedures (CRREL)	09/95
8. Characterize products of microbial degradation (WES)	09/95
9. Evaluate effects of clay type on interactions with explosives (WES)	09/95
10. Determine microbial mutagenicity and conduct *in vitro* assays (WES)	09/95

11. Determine conjugation kinetics (Natick) 09/96
12. Determine precision and accuracy of analytical method in various matrices (CRREL) 06/96
13. Identify factors controlling biodegradation of conjugates (WES) 09/96
14. Determine bioavailability of explosives after interaction with clays 09/96
15. Conduct whole organism and early life stages bioassays (WES) 09/96
16. Characterize organic conjugates from natural soils (Natick) 09/97
17. Determine ruggedness of analytical method (CRREL) 09/97
18. Determine environmental factors affecting interactions with clays (WES) 09/97
19. Determine effects of environmental factors on toxicity (WES) 09/97

10. Transition Plan:

Those who are developing remediation technologies will have access to results and their implications for 6.2 and 6.3a levels as they are developed through conference presentations and published reports. Direct interactions between principal investigators of this project and other relevant projects under Environmental Quality and Technology Program 6.2 remediation technology work units and SERDP work units will be initiated in the form of briefings and informal discussions.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	500	500	500	500	2000

12. Performers:

The lead laboratory for the proposed research is the U. S. Army Engineer Waterways Experiment Station who will be responsible for completion of Tasks II, IV and V. The U. S. Army Natick Research, Development, and Engineering Center will conduct Task I and contribute to Task II. The U. S. Army Cold Regions Research and Engineering Laboratory will conduct Task III. At least one cooperative agreement with a university is anticipated.

13. Principal Investigators:

Judy Pennington (Sr Principal Investigator)
Douglas Gunnison, and Vic McFarland
U. S. Army Engineer Waterways
Experiment Station
3909 Halls Ferry Road
Vicksburg, MS 39180-6199
TEL: 601-634-2802, -3873, and -3721
FAX: 601-634-3120

Thomas Jenkins
U. S. Army Cold Regions Research and
Engineering Laboratory
72 Lyme Road
Hanover, NH
TEL: 603-646-4385 FAX: 603-646-4644

David Kaplan
U. S. Army Natick Research
Development, and Engineering Center
Natick, MA 01760-5020
TEL: 508-651-5525 FAX 508-651-5521

14. Keywords:

explosives, conjugates, remediation, analytical methods, toxicology, microbiology

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup Thrust Area

2. **Title:** Integrated Biotreatment Research Program: From Flask to Field

3. **Agency:** US Army

4. **Laboratory:** USAE Waterways Experiment Station (WES)

5. **Proposal ID:** #720

6. **Problem Statement:**

The DoD has literally thousands of sites that are contaminated with organic compounds that pose a serious threat to the environment on land entrusted by the public to be properly maintained by the DoD. As part of the realization by DoD of its responsibility toward cleanup of the numerous sites contaminated from past military activities, the majority of these sites are slated for cleanup (remediation). Unfortunately, the remediation of these sites using existing technologies is problematic from an economic, technical, and political point of view. Current technologies for soil and groundwater are incineration and phase change technologies (activated carbon and air stripping), respectively. The projected costs associated with site restoration using these current technologies are astronomical. All too often because of these high costs, landfilling is selected instead of true on-site remediation. From a technical point of view, phase change technologies do not result in the on-site destruction of the contaminants posing serious disposal and transportational problems. Politically, siting of an incinerator is a publicity nightmare. Also, the US Environmental Protection Agency (USEPA) and DoD is encouraging strong investment and application of innovative technologies. Of all the innovative technologies under development and in some cases, application, biotechnologies are considered by most remediation experts to be the most promising.

Biotreatment processes have been successfully demonstrated for treatment of a variety of contaminants. Research, regulatory, and user communities collectively agree that biotreatment of easy-to-degrade compounds, such as fuels and simple phenols, are established processes. Based on the success of these biotreatment applications, a strong potential exists for development of biotreatment processes with expanded application toward more difficult to degrade contaminant groups such as explosives, chlorinated solvents, polychlorinated biphenyls (PCBs), and carcinogenic (heavy) polycyclicaromatic hydrocarbons (cPAHs). Several governmental and academic research groups are currently investigating biotreatment techniques for treatment of these traditionally difficult to degrade contaminants. Although a high potential exists for development of vastly improved remediation techniques using biological processes for remediation of media contaminated with these compounds; unfortunately, sporadic and often sparse funding and inaccessibility to actual sites have severely hindered process development. Other factors contributing to the delay of process development include poor intercommunication between research groups, the lack of design and application engineering input into research plans, and poor technology transfer to applied research and technology user groups.

This program is proposed as a new 6.2 program that will enhance, but not duplicate, existing funded efforts in the DoD STRAT Plan. This program also fits nicely into USEPA's long-term research plans. The following DoD user requirements will be met or partially met by performance of this R&D program:

1.I.1.f. Treatment system for water contaminated with organic contaminants.
1.II.1.a. Improved fate, effects, and transport models for groundwaters.
1.I.1.g. Treatment system for water contaminated with chlorinated and defense hydrocarbons.
1.I.1.j. Treatment of Navy relevant contaminants in salt/brackish/groundwater matrices.
1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
1.I.1.h. Treatment system for water contaminated with mixtures of chlorinated solvents.
1.I.1.e. Process to remediate groundwater contaminated with hydrocarbon fuels.
1.I.4.c. Decontamination of soils containing energetics materials.
1.I.2.i. Contamination under buildings and roads.
1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
1.I.3.a. Technologies for isolation and decontamination of sludges.
1.I.2.b. Dredged soil area decontamination and reclamation.
1.I.2.e. Improved marine sediment remediation technologies for metals, organics, and PCBs.
1.I.6.d. Improved shore and open Ocean hazardous materials cleanup/restoration.
2.III.1.d. Enzyme and bacterial treatment technology.
1.I.4.c. Decontamination of soils containing energetic materials.
2.III.2.d. Improved cleanup procedures at locations where UST leaked.

7. Project Description:

This project represents a collective research initiative by several key governmental and academic organizations with a long history of developing treatment technologies. All of the partnering organizations are bringing into the initiative not only experience, but additional funding and experimental resources that will be "dovetailed" into this comprehensive program. The partnering approach proposed will ensure that appropriate scientific and engineering disciplines interact to form a formidable research team of a magnitude never attempted within the DoD environmental biotreatment research program. The project will be approached through investigation of several primary technical issues. The level of research effort expended on each issue will vary depending on state of the art for that issue. The ultimate goal of this program is to perform research efforts that will result in the fielding of several biotreatment processes for remediation of predominant DoD contaminants.

The proposed experimental approach will be to first investigate a variety of promising biotreatment techniques at the bench scale. During performance of bench activities, engineers with design and implementation experience (the Baltimore COE District) will assess the overall implementation potential and projected costs associated with these techniques. This effort will ensure that the research groups are developing processes that are realistic and on firm technical ground. Upon completion of the bench efforts several small scale pilot studies (referred herein as intermediate scale) will be performed using those techniques considered most promising. After performance of the intermediate scale studies, at least four of the most economically and technically sound processes will be evaluated on the field pilot scale at actual DoD sites.

The primary technical issues to be addressed in this research initiative are listed and briefly discussed below:

Issue I. Biotreatment of Explosives Contaminated Soils and Groundwaters. A variety of promising biotreatment techniques will be investigated for remediation of soil and groundwater contaminated with explosives compounds. Explosives contamination represents one of the most prevalent organic contamination within the DoD. Although research into the feasibility of biotreatment of explosives has been undertaken by both DoD and USEPA over the last few years, funding limitations and the lack of a comprehensive research approach have hindered significant advances toward the field scale. The following biotreatment mechanisms will be investigated for explosives:

a. Enzymatic degradation performed under a variety of controlled systems. Controlled enzyme manufacturing methods will also be investigated.
b. The use of specialty surfactants, both manufactured and natural, will be evaluated for their ability to enhance the bioavailability of the explosives compounds to the microbial populations during treatment.
c. The metabolic pathways and biodegradation of key intermediates.
d. Alternating redox conditions and techniques for establishment of either condition within an active bioreactor system.
e. The use of genetically altered microorganisms as reactor seeds.

Issue II. Soils and Groundwaters Contaminated with Chlorinated Solvents. Chlorinated solvents represent a class of contaminants that is detected at more DoD sites (and CERCLA and RCRA sites for that matter) than any other contaminant group. Several significant breakthroughs in the biological degradation of these compounds have been made over the last several years; however, limited funding and access to contaminated sites has hindered further development. Issues under investigation for chlorinated solvents within this program include:

a. Bioventing of chlorinated solvents using aliphatic oxygenase pathways via addition of simple aliphatic gases (i.e. propane, methane, etc.).
b. Evaluation and modeling of enzyme production and substrate interactions.
c. Anaerobic biodegradation in aqueous and soil phase systems.
d. The impact of co-distributed solvents on biodegradation rate.
e. Bioslurry treatment using process air recirculation.

Issue III. Soils and Sediments Contaminated with PCBs. Soils and sediments contaminated with PCBs represent one of the most challenging compound groups under investigation in this project; yet, development of a viable biotreatment process could result in significant savings to the DoD. PCBs are found at many DoD installations due to improper disposal of hydraulic fluids and waste lubricating oils. Primary issues under investigation are:

a. Degradation and production kinetics of enzyme based degradation.
b. Cycling of redox conditions from anaerobic to aerobic as a means of dechlorinating higher substituted Aroclors into lower substituted, easier to degrade Aroclors.
c. Use of surfactants both natural and manufactured as a means of enhancing bioavailibity during biological treatment.
d. An evaluation of candidate cometabolites for enhanced degradation of selected PCB Aroclors.

e. Use of genetically altered microorganisms as potential seed sources.
f. The impact of other co-distributed contaminants, such as petroleum hydrocarbons, on PCB biodegradation.
g. Evaluation of various natural isolates and consortia toward PCB biodegradation using a variety of biotreatment systems.

Issue IV. Soils Contaminated with cPAHs. This group of contaminants represent the most regulated of PAH compounds due to their carcinogenic properties. Also, because of their large and complex molecular structure, they also represent the most difficult of all the PAHs to biologically degrade. Key research issues are:

a. Surfactant, both natural and manufactured, for enhancing biodegradation rate in a variety of biotreatment systems.
b. Evaluation of candidate cometabolites for initiating and economically maintaining effective cPAH biodegradation rate.
c. Use of genetically altered organisms for enhancing biodegradation.
d. Cascading aerobic bioslurry treatment.
e. Composting techniques for degradation of highly complex cPAH contaminated matrices.
f. Evaluation of various natural isolates and consortia activity toward cPAHs under a variety of implementation scenarios.

Issue V. Development and Design of Specialty Reactors. Many of the biological systems required for implementation of concepts under development in this project require specialty reactors. Periodically, the results of the various contaminant specific activities will be reviewed for determination and selection of appropriate implementational strategy and respective reactor type. As expected, the actual reactor designs will be governed by the breakthroughs and conditions dictated by the results of the above listed study issues. Expected reactor designs that to be developed are:

a. Zero-head aerobic bioreactors which utilize hydrogen peroxide as an alternative oxygen source.
b. Evaluation of solid and semi-solid oxygen sources for both *in situ* and *ex situ* strategies.
c. Cascading bioslurry systems (as mentioned above in the cPAHs section).
d. Improved process gas recirculation systems for treatment of contaminated media containing volatile compounds such as chlorinated solvents.
e. Side-stream dual aerobic reactor systems for treatment of refractory compounds and low level contaminated groundwaters.
f. Evaluation of low carbon loaded attached growth systems for treatment of low level contaminated groundwaters.
g. Development of biocells as an economically attractive reactor option.

Issue VI. Applications Potential of Genetically Engineered Microorganisms. Although science is rapidly approaching the time when genetically altered organisms may play an important part in future bioremediation processes; unfortunately, the political and social implications surrounding these organisms may hinder implementation of these organisms into reactors. This project will assess and identify problems associated with implementation of engineered organisms. A logical plan of action in terms what actions may be taken to accelerate and enhance the use of these microorganisms will be drafted.

Issue VII. Toxicity Reduction. The success of treatment will be assessed on processes selected for intermediate scale evaluation using a variety of toxicological assays used to properly quantify toxicity reductions.

8. Expected Payoff:

The primary benefit of this study is reduced remediation costs associated with development of "realistic" biotreatment processes for cleanup of contaminated DoD sites. Projected treatment costs are expected to fall at or below the $150 per cubic yard of soil treated (incineration costs are usually above $350/cy) or $1.00 per thousand gallons of groundwater treated (carbon costs are usually greater than $1.00/Kgal). Secondary benefits include; expanded implementation potential of existing and developing biotreatment processes, biotreatment technologies that result in the on-site destruction of contaminants, increased regulatory and political acceptance of DoD cleanup activities will be realized as these technologies are used, and increased user acceptance of the technologies will be realized because of the involvement of the user community (COE-Baltimore District) within the project structure.

9. Milestones:

Major milestones for this program are listed below. For each milestone listed at least a WES report will be drafted by the performing research group; however, each partner involved in the milestone will be encouraged to publish the report under their agency framework to accelerate transfer of information to the user community. The primary, completion based milestones (assuming a two year FY funding life) are:

1. Biocell field pilot scale study	9/94
2. Low level organic loaded bioreactor field pilot study	9/95
3. Field pilot scale evaluation of zero-head bioreactor	9/95
4. PAH bench scale studies	9/95
5. Report on fielding potential of engineered microbes	9/95
6. Chlorinated solvent bench studies	9/96
7. PAH intermediate scale study	9/96
8. Explosives bench studies	9/96
9. Chlorinated solvents intermediate scale studies	9/96
10. PAH field pilot study	9/97
11. PCB bench scale studies	9/97
12. Explosives intermediate scale studies	9/97
13. PCB intermediate scale studies	9/98
14. Explosives field pilot scale studies	9/99
15. PCB field scale study	9/99

10. Transition Plan:

The results of this study will be presented in a form that will easily be utilizable by AEC, COE, USEPA, and the private sector for demonstration and implementation. Efforts will be made to collaborate with private organizations for enhanced process development through CRADAs. Additional collaboration with the USEPA via the SITE program will also be investigated. Also, partnering efforts with AEC, DoD installations, and USEPA/COE will be encouraged as an additional means of technology transition.

In addition to official project reports, partners within this program will be encouraged to publish in peer reviewed journals, present information at national and international symposia, and informal briefings at DoD, COE, and USEPA offices. Additional tech transfer will be encouraged through an annual open symposia at WES where the results from this program and related partnering activities will presented by the various program partners. One final note, the efforts proposed in this program directly fit in the DoD Tri-Services STRAT plan.

11. Funding: ($K)

The funding requirements for this program and collective partnering 6.2 research funds and reimbursable funds:

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP (6.2)	2450	3950	3250	3500	3250	16400
USA	1500	1250	800	1000	500	5050
USAF	500	500	100	0	0	1100
USN	500	300	300	0	0	1100
USEPA	1500	1500	500	100	100	3700
DOE	500	500	500	500	500	2500
GLRC	300	300	200	200	0	1000
TOTAL	7250	8300	5650	5300	4350	30850

12. Performers:

The partners for this research initiative are listed below. Under each partnering agency, at least one point of contact is presented. Letters from each party expressing interest with their involvement in this program are enclosed. Detailed technical approaches and levels of activity will be presented if a detailed proposal is requested for SERDP-SA Board review.

Mr. Mark Zappi
Dr. Doug Gunnison
Dr. Judy Pennington
USAE Waterways Exp. Sta.
Vicksburg, MS

Dr. Joanne Jones-Meehan
Naval Surface Warfare Center
Dahlgren, VA

Dr. Steve McCutcheon
USEPA-Env. Res. Lab
Athens, GA

Dr. Jim Spain
Ms. Cathy Vogel
Armstrong Lab
Tyndall Air Force Base
Panama City, FL

Dr. Sabine Apitz
USN-Navy/NRAD
San Diego, CA

Dr. John Wilson
USEPA-R. S. Kerr Lab
Ada, OK

Dr. Hap Pritchard
USEPA-Env. Res. Lab
Gulf Breeze, FL

Ms. Chris Correale
USAE Baltimore District
Baltimore, MD

Dr. Jim Johnson (Howard University)
Dr. Walter Weber (U. of Mich.)
Great Lakes and Mid-Atlantic Hazardous Substance R&D Center
Ann Arbor, MI

Dr. David Kaplan
US Army-Natick R,D, and E Center
Natick, MA

13. Principal Investigator:

Mr. Mark E. Zappi, P.E.
CEWES-EE-R
USAE Waterways Experiment Station
3909 Halls Ferry Rd.
Vicksburg, MS 39180
TEL: 601-634-2856
FAX: 601-634-3833

14. Keywords:

Biotreatment, explosives, polychlorinated biphenyls, chlorinated solvents, polycyclicaromatic hydrocarbons, bioreactors

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Cleanup

2. Title: Surfactant-Enhanced Biodegradation of Contaminants

3. Agency: Army

4. Laboratory: WES

5. Proposal ID: #731

6. Problem Statement:

Overall Goal: This research will investigate the basic processes limiting the bioavailability of contaminants sorbed to soils and evaluate the applicability of biologically-mediated, desorption-enhancing processes to increase microbial destruction of these contaminants.

Problem Statement: The DoD has sites contaminated with a variety of energetic and organic compounds. Long-term persistence of these materials in soils is directly related to poor mobility of the contaminants and to resistance of the contaminant to microbial degradation. Many of these organic contaminants are sorbed onto clays or organic matter in soils. Through a combination of sorption processes, the contaminant may move deep into soil pores and/or clay mineral lattice structures, effectively immobilizing the contaminant. Inability of sorbed contaminants to partition back into the aqueous phase severely limits microbial degradation of contaminants in soil treatment systems. Correspondingly, effective biotreatment for those compounds is impaired because the bacteria are unable to contact the sorbed compound. As a result of these processes, immobilization is a significant problem to overcome in site restoration.

Mobilization of contaminants is highly desirable for the development of new remediation technologies and improvement of existing technologies. For example, initial research at the U.S. Army Engineer Waterways Experiment Station (WES), the U.S. Environmental Protection Agency Athens Environmental Laboratory (AERL), and the U.S. Naval Surface Weapons Center (NSWC) indicates that certain surfactants can accelerate microbial degradation of TNT and chlorinated aromatic hydrocarbons and that microorganisms produce bioemulsifiers that may promote removal of contaminants previously bound to the soil. Other investigations indicate that enzymes modify certain contaminants that strongly sorb to soil, altering their affinity for soil by modifying the structure of substituents on the contaminant molecule. As a result, an intermediate transformation product having increased solubility may be produced, thus enhancing complete microbial degradation of the contaminant.

Enhancing the effectiveness of bioremediation will require an integrated investigation of the physical, chemical, and biological factors affecting sorption of organic contaminants as they relate to bioavailability. The information gained from this 6.1 level basic research can be directly applied to 6.2 level investigations to promote bioremediation technologies.

Project Objectives: Determine the role of sorption on availability of contaminants to microbial degradation. Reduce costs for microbial treatment of soils in sites contaminated

with explosives and other organics by identifying ability of microbially-supported, desorption-enhancing processes to overcome sorption limitations.

Status of Project: Research was initiated to identify basic sorption processes and determine their possible relationship to microbial degradation of contaminants under SERDP in FY 93. This proposed basic research will further develop that effort in conjunction with preliminary work supported under the Environmental Quality and Technology Program. This research is jointly submitted by the US Army (WES) and the US Navy (Naval Surface Warfare Center) and US EPA (ERL-Athens) for SERDP funding.

7. Project Description:

Technical Objectives: Determine the significance of soil sorption on biological availability of representative explosives, chlorinated pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Provide procedures to determine the most effective means by which microorganisms overcome sorption limitations. Develop methods to determine applicability of microbiologically-mediated, desorption-enhancing processes to improve microbial destruction of contaminants. Provide this information in a form suitable for use at the 6.2 level.

Technical Approach: Determine the importance of sorption in controlling bioavailability of several organic contaminants of military importance and identify the means microorganisms utilize to overcome these limitations. This will be accomplished in a series of tasks listed below. Critical portions of Tasks II, III, and IV require application of several microbiological and biochemical technologies that are at the cutting edge of present-day research. For this reason, the proposed research could not have been undertaken 2-3 years ago.

a. Task I. Compare diffusion of organic contaminants within soil particles with microbial degradation to determine limiting rates and focus research on the more significant knowledge gaps. Identify suitable systems in which to study processes. Determine presence or absence of biosurfactant and/or bioemulsifier production by key microbial species active in contaminant degradation. Identify the potential for alteration of sorption properties and bioavailability through reductive modification of contaminant structures.

b. Task II. Develop techniques for investigating sorption sites on and diffusion within soil particles. Develop techniques for investigating movement of microorganisms producing biosurfactants and/or bioemulsifiers and reductive processes having sorption-modifying capabilities.

c. Task III. Develop predictive sorption kinetics models to evaluate importance of sorption to bioavailability and select the most appropriate procedures for determining sorption limitations. Develop a data base for verification of general predictive techniques with soils having a wide range of properties.

d. Task IV. Develop a protocol to determine most effective means for enhancing microbial accessibility with site specific soils. Verify protocol with microorganisms and contaminants in various biological treatment systems.

e. Task V. Draft Implementation Protocol. Develop a draft implementation protocol detailing the following:

(1) Procedures for determining impacts of sorption on microbial availability, including equipment, chemicals, and methods.

(2) Guidance on how to interpret results.

(3) Guidance for application of predictive techniques. Descriptions of procedures to evaluate ability of microbial processes to overcome sorption limitations.

(4) Develop technology transfer documents, seminars, and laboratory, demonstrations to transition the technology to 6.2 level. Where appropriate, supply technology in a form suitable for direct application to 6.3 level.

Relationship to DoD/EPA Environmental Objectives: Information obtained from the performance of this study will contribute to several DoD/EPA environmental remediation objectives. This work will improve contaminant destruction technology by enhancing bioavailability of contaminants sorbed to soil. Specific user requirements that will benefit from performance of this work include:

(1.I.1.b) Technology for removal of energetics/other organics contamination (A,N)()(F)

(1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)()(F)

(1.I.2.i) Contamination under buildings and roads (A,N,AF)()(F)

(1.I.4.n) Remedial treatment technology for soils contaminated with chlorinated and nonchlorinated organics (A,N,AF)()(F)

(1.I.1.i) Technique to maximize contaminant withdrawal with minimum water treatment (A, N, AF)()(F)

8. Expected Payoff:

Potential Users: DoD, DOE, private Superfund, and RCRA site managers will benefit from procedures to enhance bioremediation. Development of this technology will allow cost-effective in-situ and landfarming biotreatment of soils and sediments contaminated with explosives and other organic compounds. Current soil incineration techniques destroy local ecosystems. The technology will also benefit ex-situ techniques, such as bioslurry reactor treatment. This will be especially important at those sites where microbial destruction of crystalline TNT is required.

Positive Impacts: This study will integrate technology development and basic research to provide better means to develop the most cost-effective treatment options. Rapid determination of factors affecting microbial accessibility to contaminants has the potential to decrease the overall costs of in-situ, landfarming, and bioslurry treatment of contaminated soils.

9. Milestones:

Major milestones under this work effort are listed below, along with the respective month and year they will be completed.

1.	Initial comparison of desorption and biodegradation rates for typical soils (Task I)	09/94
2.	Identify systems in which to study processes (Task I)	12/94

3. Investigate biosurfactants and bioemulsifers (Task I) 03/95
4. Determine effects of chemical structural modification on desorption (Task I) 09/95
5. Develop innovative experiments to quantify sorption sites and diffusion between particles (Task II) 12/95
6. Evaluate movement of microorganisms into soil structures (macropores) (Task II) 03/96
7. Select and document the microorganisms producing successful biosurfactants and bioemulsifiers (Task I) 06/96
8. Develop and verify predictive desorption and microbial degradation models (Task III) 09/96
9. Develop protocol to enhance microbial accessibility (Task IV) 12/96
10. Examine abilities of microorganisms to produce surfactants and emulsifiers in test systems (Task IV) 03/97
11. Develop general purpose predictive sorption kinetics models (task III) 06/97
12. Verify predictive techniques for desorption enhancement in selected soils (Task III) 09/97
13. Develop protocols for enhancing microbial accessibility (Task IV) 12/97
14. Document predictive models for sorption (Task III) 09/98
15. Write final guidance for desorption enhancement (Task V) 03/99
16. Conduct technology transfer seminars and workshops (Task V) 09/99

10. Transition Plan:

This 6.1 level research will directly support bench-scale assessments at the 6.2 level. As work progresses, briefings and direct input by principal investigators will be provided to relevant Environmental Quality and Technology Program 6.2 level biotreatment work units and corresponding work units in the environmental programs of other agencies. In addition, the proposed work will directly support the work developed in the Integrated Biotreatment Research Program SERDP proposal developed by WES. Technical assistance for these purposes will be available during and after the course of the research. The technology will also be transferred through technical papers, presentations, and work unit reports. Professors, post-doctorals and graduate students will be involved in helping to develop the studies and conduct the work, which will indirectly aid education. We will also consider application of this technology to suitable field scale technologies through use of cooperative research and development agreements (CRADAs).

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP (6.1)	700	800	900	950	850	700	4900
WES	350	400	400	350	350	325	2175
AERL	300	300	300	300	300	300	1800
NSWC	150	150	150	150	125	100	825
TOTAL	1500	1650	1750	1750	1625	1425	9700

12. Performers:

The lead laboratory for the proposed research will be the U.S. Army Engineer Waterways Experiment Station (WES). WES will make contributions to all the tasks and have responsibility for Tasks II, IV, and V. The NSWC Biotechnology Laboratory, Silver Springs,

MD will have responsibility for Task I and will make major contributions to Tasks II and III, plus some contribution to Task V. AERL will make some contributions to Task I, major contributions to Tasks II-V and have primary responsibility for Task III. The NSWC will continue cooperative work with the University of Maryland; AERL will conduct some research on desorption kinetics and biodegradation with competitive cooperative agreements. WES and AERL will work with either the Hazardous Substance Research Center/South and Southwest or the Hazardous Substances Research Center/West. WES may also work with Texas A&M in its University Research Initiative with the Army Research Office. WES personnel will interact directly with university personnel through the Visiting Professor Program, with the National Research Council Post Doctoral Program, and by direct contracts between WES and graduate students.

13. Principal Investigators:

Dr. Douglas Gunnison (Senior Principal Investigator)
Dr. Judith C. Pennington
US Army Engineer Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, MS 39180-6199
TEL: (601) 634-3873 and -2802 respectively
FAX: (601) 634-3120

Dr. John Rogers (POC for AERL)
960 College Station Road
Athens, GA
TEL: (706) 546-3592
FAX: (706) 546-3252

Dr. Joanne Jones-Meehan (POC for NSWC)
10901 New Hampshire Avenue
Silver Spring, MD 30903-5000
TEL: (301) 394-4839
FAX: (301) 394-4841

14. Keywords:

Mineralization; Sorptive Processes; Bioavailability; Surfactant; Reduction

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** Cleanup of TRU Contaminated Soils with CO_2 Soluble Ligands

3. **Agency:** Department of Energy

4. **Laboratory:** Idaho National Engineering Laboratory (INEL)

5. **Proposal ID:** #447

6. Problem Statement:

The overall goal of the project is to evaluate a new class of actinide complexants for their ability to do soil and debris cleanup. The compounds are fluorinated diketones and were designed and synthesized at the University of Idaho as actinide complexants which are soluble in supercritical carbon dioxide.

Supercritical fluid extraction offers many advantages over conventional solvent extraction, including the minimization of organic liquid wastes, and exposure of personnel to organic vapors. Carbon dioxide is the fluid of choice because of its moderate critical constants, inertness and availability in purified form.

It is well known that some DOE and DoD sites have soils and debris contaminated with uranium and transuranium actinide elements. The currently envisioned treatments involve excavation and burial of soils and debris, leaching with acids, and in-situ vitrification. The first merely relocates contaminated soils and debris. Leaching or washing generates large volumes of liquid waste and generally destroys the properties of soils, leaving them sterile. Additionally, some plutonium oxides have limited acid solubility. In-situ vitrification immobilizes the actinides but also destroys the soil.

Supercritical CO_2 combines gaseous and liquid properties and allows penetration of porous substances such as soils or other debris. Thus it is a medium ideally suited to delivery of complexants to selectively remove contaminants from solids. No liquid waste is generated, when the CO_2 is depressurized the solid actinide complex precipitates. Until recently, no metal complexants were available with sufficient solubility in CO_2 to be practical for actinide extraction. Now however such compounds have been synthesized but remain to be evaluated. This new program comes under the category: Applied Research.

7. Project Description:

The technical objective is to demonstrate the range of conditions over which fluorinated, carbon dioxide soluble, diketones are useful as actinide extractants for soil and debris cleanup. To our knowledge no CO_2 soluble ligands have ever been evaluated for transuranium element extraction. Some work has been done for mercury, the lanthanides and uranium. It has been shown that a synergistic effect is exhibited when TBP is used in conjunction with the diketones, which increases actinide extraction efficiency. This effect would also be investigated.

The project would be divided into two phases. In phase I the ligand is evaluated for ability to extract actinides in several oxidation states (III, IV, V, VI) over a wide range of pHs from conventional aqueous media. Additionally, metals common to soils, such as Ca(II), Fe(III) and the rare earths would be evaluated to determine selectivity for actinides over natural soil components. This phase will determine the likelihood of the practical use of these ligands without the expense of using supercritical fluid extraction equipment. In phase II the work would be repeated in supercritical CO_2, using actinide spiked soils. Solubilities of the actinide-ligand complex would be evaluated at various temperatures and pressures to select optimum conditions. Each phase is expected to last approximately one and one half year.

8. Expected Payoff:

If this effort is successful a data package will exist which may be used to perform engineering design of a prototype for decontamination of TRU soils and debris from DOE and DoD sites. Decontamination would occur without generation of the large volumes of solid and liquid waste characteristic of excavation for burial or soil washing and without destruction of soils as is seen in acid leaching and in-situ vitrification. The actinides would be collected in a small solid volume for disposal. Industrial supercritical CO_2 extraction is already being performed in industry, usually for extraction of organics (such as caffeine from coffee) so insurmountable engineering barriers for soil or debris extractions are not expected. Private interest in marketing rights to such technology is anticipated.

9. Milestones:

a.	Complete evaluation of actinide distribution ratios in aqueous media for the common oxidation states.	3/95
b.	Acquisition of supercritical CO_2 extraction equipment for hot work.	3/95
c.	Complete evaluation of solubilities of actinide complexes in CO_2 versus temperature and pressure.	6/96
d.	Delivery of data package which would allow engineering design of prototype.	6/96

10. Transition Plan:

Attention will be drawn to the technology through journal publications and/or conference presentations, as appropriate. It is envisioned that there will be significant commercial interest in the technology.

At this time, the University of Idaho, where the CO_2 soluble ligands were synthesized, is interested in collaborative evaluation of their properties. The INEL contribution is pre-existing facilities amenable to actinide research, and personnel experienced with actinide handling and chemistry. Dr. Chen Wai is the university contact.

This collaborative effort should enhance credibility and interest in the program from private industry. Following any engineering design of a prototype a CRADA would be attempted with an environmental remediation company.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	50	75	10	135
DOE	50	75	10	135

12. Performers:

Idaho National Engineering Laboratory and the University of Idaho.

13. Principal Investigator:

Bruce J. Mincher
INEL
P. O. Box 1625
Idaho Falls, ID 83415-7111
Phone: (208) 526-4449
FAX: (208) 526-7069

14. Keywords:

Supercritical Fluids, Actinide Extraction, Supercritical Carbon Dioxide, Fluorinated Ligands, Metal Chelation, Actinide Supercritical Fluid Extraction

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Cleanup

2. Title: Fuel Hydrocarbon Remediation

3. Agency: Navy

4. Laboratory: Naval Facilities Engineering Service Center

5. Proposal ID: #020

6. Problem Statement:

Fuel-contaminated water and soil remediation technologies evaluation is one of several thrusts managed under the umbrella of the National DoD Environmental Technology Demonstration Program initiative started in FY93. This demonstration program supports SERDP program efforts to meet DoD environmental obligations, and reduce the future life-cycle costs associated with cleanup and compliance with environmental regulations. Success will be measured by ability to meet cleanup levels, acceptance by regulators, and by transferring technologies with performance data and design guides to industry.

The goal is to achieve regulatory and institutional acceptance of, and transfer to industry, innovative remediation technologies for fuel contaminated water, sediments and soils. The most common fuel contaminated sites within DoD are those with jet fuels (JP-5), marine diesel, gasoline and bunker fuel. These sites are located near underground storage tanks (UST), fuel farms and other locations where spills have occurred resulting in extensive fresh and brackish surface and groundwater contamination, and sediments and soil contamination.

Remedial action at these sites are often complicated. This is due to numerous UST excavation sites being in areas of shallow water tables overlying brackish water, and others with fresh water containing high dissolved solids. Some of these site are located in extreme geologic and climatic conditions. This effort applies to the DoD Cleanup Pillar, Requirement Thrusts 1.N: Treatment of Fuels in Soil and 1.J: Treatment of Fuels in Groundwater, as identified in the Tri-Service Environmental R&D Strategic Plan.

This is an on-going 6.3 effort which began with FY93 SERDP funds.

7. Project Description:

The objective of the National DoD Environmental Technology Demonstration Program for fuel contaminated water and soil is to conduct side-by-side field demonstrations comparing advanced technologies under similar conditions. The DoD requirements being addressed are (1.I.1.e) Process to Remediate Groundwater Contaminated with Hydrocarbon Fuels and (1.I.4.m) Process to Remediate Soils Contaminated with Hydrocarbon Fuels.

Demonstration projects will test innovative remediation treatment train technologies at ex-situ soil and sediments treatment site(s), ex-situ surface and groundwater treatment facilities, and in-situ soil, sediments and groundwater treatment site(s) in a wide range of climatic conditions. Candidate technologies selected within specific treatment method areas will be

technologies emerging from DoD laboratories as identified in the Tri-Service Environmental Quality Research and Development Strategic Plan, and Broad Agency Announcement (BAA) solicitations. Projects from the EPA SITE Technology and Demonstration program may also be candidates for demonstration. Emerging technologies such as the following proposed projects will be demonstrated:

Bioremediation technology (Phase I) will be demonstrated using soil contaminated with different types of fuel. This will include gasoline, diesel, JP-5 and possible combinations of these hydrocarbons. The technical objective is to determine biocell and nutrient feed design parameters. In this innovative biocell demonstration, highly mobile nutrient mixtures will be evaluated with respect to optimizing native soil hydrocarbon degrading microorganisms to quicken the pace of cleanup. A Broad Agency Announcement (BAA) solicitation is underway to obtain proposals concerning emerging remediation technologies. A multi-disciplinary Advisory Committee (AC) to the fuel hydrocarbon contamination remediation National Test Site manager will evaluate the proposals and recommend a candidate method for contract award. Because of uncertainties with regard to dynamic living organisms, and environmental factors which influence these systems, low-to-moderate risk is associated with the bioremediation effort.

Bioremediation has been field studied for a number of years. Biological treatment processes investigated have used indigenous or selectively cultured bacteria and/or fungi. Some biological processes studied used existing soil conditions while other studies, including this effort, altered/enhanced environmental factors influencing microorganism transformation of hazardous waste with changes in pH, temperature, oxygen concentration, and availability of essential nutrients, and soil structure.

The enhanced bioremediation project demonstration for ex-situ treatment of fuel-contaminated soil is being conducted at the Naval Construction Battalion Center (NCBC), Port Hueneme, California. This site is one of the National DoD Environmental Technology Demonstration Program fuel and solvent remediation demonstration sites.

In Phase II and onward, other technologies, or treatment trains, will be evaluated at fuel and solvent remediation demonstration sites including in-situ and ex-situ decontamination treatment of soil and groundwater with brackish and high dissolved solids content. Demonstrations will be prioritized and scheduled in five phases. Each demonstration project will last approximately two years. These technologies will be identified and selected by a multi-disciplinary an NTS Advisory Committee. Candidate projects may come from emerging modifications to treatment trains such as the following areas: (1) thermal or chemical enhanced soil vapor extraction, (2) soil flushing and washing amendments, (3) chemical catalytic reduction/oxidation mixed product recovery, (4) emission controls for low temperature thermal desorption, and (5) free product recovery.

Because of uncertainties with regard to potential responding organizations and companies, low-to- moderate risk is associated with these remediation projects.

8. Expected Payoff:

Field and laboratory data collected will be incorporated into a Tri-Service Data Package to develop life-cycle cost information and design engineering guidelines. Those technologies transferred would reduce remediation costs, accelerate the pace of cleanup, and facilitate

compliance with various Federal and State regulations in order to protect human health and the environment. The transfer of critical technologies into full scale implementation is an integral and strategic part of the DoD environmental objective.

The data presented in technology transfer media will be comparable with data from other DoD, EPA and DOE SERDP projects. Technology transfer involves dissemination of information within the DoD engineering and environmental organizations which are making remedial action decisions and external transfers to industry and other Federal, State and Municipal organizations evaluating those decisions or implementing the technologies. Major benefits resulting from these technology demonstration projects are applicable and transferable to a large number of DoD sites reducing the cost associated with site demonstrations and the time needed to remediate sites.

9. Milestones:

Phase I: Ex-situ soil treatment

1. Obtain project approval from AC	01/94
2. Complete contract award	04/94
3. Complete site plans (QA/QC, safety, demo)	05/94
4. Complete peer review of plans	06/94
5. Obtain permits	05/94
6. Complete excavated soil characterization	05/94
7. Complete final design	05/94
8. Construct Test I remediation cells	06/94
9. Initiate Test I field demo	06/94
10. Complete first monthly sampling	07/94
11. Complete Test I remediation field demo	10/94
12. Construct Test II demo system	11/94
13. Operate Test II system	12/94
14. Complete first monthly sampling	01/95
15. Complete Test II demo	04/95
16. Demobilize demo system	05/95
17. Complete TE&DG documentation	08/95

Phase I: Ex-situ treatment (TBD)

1. Complete Broad Agency Announcement	04/94
2. AC review and technology selection	06/94
3. Complete contract award	08/94
4. Complete site plans(QA/QC, safety, demo)	11/94
5. Complete peer review of plans	12/94
6. Obtain permits	12/94
7. Complete soil characterization	12/94
8. Complete final design	01/95
9. Complete setup & startup	02/95
10. Complete 2nd technology demonstration	07/95
11. Complete TE&DG documentation	09/95
12. Complete Phase I tech transfer package	02/96

Phase II: Ex-situ treatment of contaminated groundwater	
1. Complete Broad Agency Announcement	05/95
2. AC review and technologies selection	09/95
3. Complete contract(s) award	11/95
4. Complete site plans	02/96
5. Complete peer review of plans	04/96
6. Obtain permits	05/96
7. Complete groundwater characterization	05/96
8. Complete final design	06/96
9. Complete setup & startup	07/96
10. Complete field demo (2 technologies)	01/97
11. Complete Phase II TE&DG documentation	04/97
Phase III: In-situ remediation of soil, sediments and groundwater	
1. Complete BAA/peer review selection	10/95
2. Complete contracts for Phase III	04/97
3. Complete start up Phase III demonstrations	09/97
4. Complete Phase III demonstrations	06/98
5. Complete Phase III tech transfer package	09/98
6. Complete NTS program evaluation report	02/99
Phase IV: Emerging Technologies	
1. Complete BAA/peer review selection	10/97
2. Complete contracts for Phase IV	02/98
3. Complete start up Phase IV demonstrations	05/98
4. Complete Phase IV demonstrations	04/99
5. Complete Phase IV tech transfer package	08/99
Phase V: Emerging Technologies	
1. Complete BAA/peer review selection	10/98
2. Complete contracts for Phase V	02/99
3. Complete start up Phase demonstrations	05/99
4. Complete Phase V demonstrations	04/00
5. Complete Phase V tech transfer package	08/00
6. Decommission site	12/00

10. Transition Plan:

At the completion of each field demonstration, a technology transfer package which includes an Technology Evaluation & Design Guidance document will be prepared and disseminated within organizations (DoD, DOE, EPA) which are making remedial action decisions. These technologies will be transferred to industry and other Federal, State and Municipal organizations for implementation at multiple DoD sites Nation and World wide. The National DoD Environmental Technology Demonstration Program Test Organization is responsible for a multi-media technology transfer package that will include: (1) technical short courses/seminars, (2) on-site visitor's workshops, (3) field assistance, (4) conference exhibits and (5) demonstration videotapes and brochures. The principal investigator/project officer will develop professional journal articles.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	FY00	Total
SERDP	895	550	800	800	900	900	900	800	6545

12. Performers:

The field bioremediation demonstration will be conducted by Mr. Ms. Leslie Karr from the Naval Facilities Engineering Service Center (NFESC). Ms. Leslie Karr, NFESC, will be the principal investigator/coordinator for Phase II Emerging Technologies projects. DoD laboratories as identified in the Tri-Service Environmental Quality Research and Development Strategic Plan, and Broad Agency Announcement (BAA) solicitations will be used to solicit proposals for demonstration projects. A peer review panel will review proposals and recommend contract award for a specific method.

13. Principal Investigator:

Ms. Leslie Karr, Project Officer
Naval Facilities Engineering Service Center
ESC411, 560 Center Dr.
Port Hueneme, CA 93043-4328
TEL: (805) 982-1299
FAX: (805) 982-1409

14. Keywords:

Remediation, Fuels, Demonstrations (remediation technology), Treatment, Soil (decontamination), Groundwater (decontamination)

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Cleanup

2. **Title:** National Environmental Technology Demonstration Program

3. **Agency:** Army

4. **Laboratory:** Army Environmental Center (AEC)

5. **Proposal ID:** #723

6. **Problem Statement:**

The current process for gaining acceptance of cost effective innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and an information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/ evaluation/transfer program.

The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation transfer program. The goal is to provide locations for comparative demonstration and evaluation of cost effective and innovative technologies to enable transfers from research to full-scale use.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the agencies based on the findings from the first objective; (3) develop test locations for the demonstration and evaluation of innovative technologies under comparable and well characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

The D/NETDP not only joins DoD agencies and the EPA, but also seeks to partner with the following programs and organizations: Advanced Applied Technology Demonstration Program for Environmental Technologies; the Environmental Performance Cooperative, Inc; the Public Private Partnerships sponsored by the EPA and executed by Clean Sites, Inc.; the Western Governor's Association; the Hazardous Substance Research Centers; the Remedial Technology Development Forum; the Federal Remedial Technologies Roundtable; the Environmental process Improvement Center; Lawrence Berkeley National Laboratory; Michigan Department of Natural Resources; Michigan Department of Commerce. This project is a continuation of an FY93 funded SERDP project entitled "National DoD

Environmental Technology Demonstration Program". Problem statements specific to each participant in this program are discussed below.

Air Force. The U.S. Air Force will develop the DoD/National Environmental Technology Demonstration Program Controlled Release Site. This facility will provide a site where research can be conducted on the transport of dense nonaqueous phase liquid (DNAPL) contamination in groundwater and where remediation technologies for DNAPLs in soil and groundwater can be demonstrated. Current environmental cleanup technologies for the cleanup of DNAPLs are costly, slow, and largely ineffective. This program will provide a test bed for research to fully understand the mechanisms in proposed treatment processes and to develop innovative treatment solutions.

In addition to the controlled release site, McClellan AFB, California will provide sites for demonstration and evaluation of solvent remedial technologies. The Air Force has many site contaminated with solvents due to past maintenance operations. Contaminated areas at McClellan AFB have been characterized, and some monitoring wells installed. Program managers, who will solicit demonstration participation and manage the overall use of on-base sites, will be provided along with development of a computer data transfer system to disseminate information on the demonstrations to all potential users.

Army. The U.S. Army is forming a national test center for explosives and heavy metals contamination at Volunteers Army Ammunition Plant (VAAP). The contamination of soil, sediments and groundwater by explosives and heavy metals has become a problem at many industrial facilities due to past disposal practices. Research in this area is in progress at several facilities under the management of separate Federal Agencies and private contractors. Currently, there are no facilities dedicated to long-term demonstrations of technologies developed from this research. The test centers will provide characterized locations together with the infrastructure required for technology demonstration. Dedicated sites will enable better use of resources since site selection and characterization will no longer be required for each new technology demonstration. With the inclusion of private technology demonstrations, regulators, users, and the public, these sites will provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector.

Navy. The U.S. Navy will demonstrate remediation technologies for the treatment of Navy-specific fuels contamination. The most common contaminants within DoD are fuels (such as jet fuels (JP-5), marine diesel, gasoline, and bunker fuel). Contaminated sites are located near underground storage tanks (UST), fuel farms, and other locations where spills have occurred resulting in extensive freshwater,brackish water, groundwater, and soil contamination. Remedial actions are complicated because numerous UST excavation sites are in areas of shallow water tables, some are in brackish water and other areas are in fresh water containing high dissolved solids. Some of these sites are located in extreme geologic and climatic conditions. This demonstration program supports the SERDP effort to meet DoD environmental obligations and reduce future life-cycle costs associated with cleanup and compliance with environmental regulations.

EPA. The EPA through the University of Michigan's Department of Civil and Environmental Engineering is implementing and operating a national field center for research and development of advanced remediation technologies. Processes which integrate biological and physicochemical processes are targeted for investigation and development. Costs for

technologies of this type are generally much lower than for alternative processes. Moreover, they can often be performed in-situ, thus further enhancing their environmental compatibility. Demonstrations conducted to date have not provided the information required to successfully translate laboratory science into effective and reliable practice. For the most part such studies have not been carried out under sufficiently well planned, controlled, and monitored conditions. They have thus yielded very site-specific information having limited value for potential remedial solutions under dissimilar conditions.

The U.S. EPA's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) is the Agency's lead laboratory for characterization and monitoring technologies. EMSL-LV's role in this project will be to coordinate the demonstration, testing, and evaluation of innovative and alternative monitoring and measurement technologies. The test beds to be used for demonstrating monitoring and measuring technologies will be the test locations established by the Services for the D/NETDP program. Technologies that can be used to measure or monitor the chemical and physical characteristics of contaminated sites are critical to the success of the overall cleanup. Further, measurement and monitoring activities conducted concurrently during remediation improve its cost effectiveness by helping to identify areas most in need of remediation by providing feedback on the success of the remediation. New characterization and monitoring technologies are critical in meeting the DoD's need to conduct cost-effective cleanups. Users, developers, and regulators want and need sound performance information and assurances about the acceptability of innovative environmental technologies.

7. Project Description:

Technical Objective. The overall technical objective of this program is to integrate and coordinate the development of test locations among the participating organizations in order to foster common methodologies for testing, cost and performance data collection, technology assessment, and information dissemination.

Technical Approach. The approach of each of the Service's test sites are in the following paragraphs.

Air Force. The U.S. Air Force controlled release test site will provide the infrastructure to allow an environmentally safe controlled release of DNAPLs. It will include test cells enclosed with sheet piling and fitted with a water pumping system to simulate the uninterrupted flow of an aquifer. There will also be monitoring wells inside and outside of the cells. These wells along with other characterization technologies will be used to track the movement of the DNAPL following its release, identify the locations where in-situ remediation technologies should be applied, and provide data on the effectiveness of the remediation technology. The primary technical difficulties associated with this project are the identification of the locations of pools of DNAPL, once they sink into the aquifer, and the subsequent verification that the remediation technology applied was effective in removing the contaminant. The selection of the controlled release site is underway. Military installations are receiving priority emphasis because of the relative ease of access; however, non-military sites could also support this project.

The McClellan AFB test sites offer unique demonstration opportunities. Some areas have soil depths over 80 feet so interference from groundwater on soil remediation technologies can be avoided. Vapor extraction wells which will support ex-situ air treatment technology

demonstrations have been installed. The computerized data transfer network being developed by McClellan AFB will link the test site with the Technology Transfer Division in the Air Force Center for Environmental Excellence (AFCEE). This office is responsible for providing consultation and recommendations for cleanup technologies to Air Force major commands and bases. The Air Force portion of this program addresses Cleanup Pillar, 1.I: Treatment of Solvents in Groundwater and Cleanup Pillar, 1.M: Treatment of Solvents in Soil of the Tri-Service Environmental Quality Strategic Plan.

Army. The DoD/National Environmental Technology Demonstration Program for Explosives and Heavy Metal Contamination is preparing the first location, Volunteer Army Ammunition Plant, with FY93 funding. In addition, the Army is selecting another installation with differing hydrogeologic conditions. Preparations for these test locations include NEPA document preparation, detailed site characterization, development of an onsite laboratory, installation of utilities, preparation of site safety plans, and determination of the requirements for test site restoration. There will be a technology selection committee of explosives or heavy metal experts (depending upon the contamination) to identify the technologies for demonstration. The criteria will include the maturity of the technology applicability to DoD needs, potential to meet established clean up levels, and potential cost savings over currently used technologies. Selected technologies can come from U.S. Army Corps of Engineer laboratories, or from private firms under Broad Agency Announcement solicitations or Cooperative Research and Development Agreements. This program applies to Cleanup Pillar, 1.G: Treatment Technology for Explosives Contaminated Groundwater; and Cleanup Pillar, 1.K: Treatment Technology for Explosives Contaminated Soils of the Tri-Service Environmental Quality Strategic Plan.

Navy. The U.S. Navy has formed a multi-disciplinary peer review panel to prepare a Long Range Plan which will provide a "road map" that identifies treatment method knowledge gaps and technology thrusts to resolve those deficiencies. Recommendations from this panel will be used to develop a phased schedule for demonstrations. This demonstration program incorporates field scale enhanced remediation technology demonstrations that can cleanup water and soil with different types of fuel contamination, including gasoline, diesel, bunker fuel, and jet fuel (JP-5); and possible combinations of these hydrocarbons. Candidates technologies within specific treatment method areas selected would be emerging from DoD laboratories as identified in the Tri-Service Environmental Quality Research and Development Strategic Plan and Broad Agency Announcement (BAA) solicitations. The Navy program addresses Cleanup Pillar, 1.J: Treatment of Fuels in Groundwater and Cleanup Pillar, 1.N: Treatment of Fuels in Soil in the Tri-Service Environmental Quality Research and Development Strategic Plan.

EPA. This project is developing a control field test-bed facility and capacity for conducting investigations required to develop, evaluate, and establish a general basis for the design and engineering of effective integrated bioremediation systems. The project will develop, evaluate, and enhance the design of integrated biologically-centered remediation technologies. The project focuses principally on in-situ remediation of surface soils, subsoils, surface waters, and groundwater contaminated by organic materials typically disposed of or accidentally spilled at military installations and energy development sites. The recently decommissioned Wurtsmith AFB in Oscoda, MI is under development as the field site for the program.

The EPA, through the EMSL-LV, will: (1) focus on assisting developers in demonstrating characterization and monitoring technologies; (2) validate the performance data, and; (3) transfer information and provide support on new technologies to the user and developer communities. Establishing this program requires establishing MOUs among appropriate agencies; developing operational guidelines; establishing a regulatory selection criteria; developing and implementing demonstration protocols; developing technology validation criteria; developing a standard data reporting format; and developing a strategy for managing and distributing information.

In addition to the approaches outlined individually for the three Services, the D/NETDP will develop technology demonstration plans to identify testing protocols, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer methods. The technology demonstration plans will be a common link among the Services to expedite the development of better, more efficient cleanup technologies. The technical risks associated with the development and management of test location are low.

8. Expected Payoff:

By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government. However, of greater interest here, are the more immediate benefits that can be derived from an integrated demonstration and evaluation program. These payoffs include (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) technology demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

9. Milestones:

	Test location availability	Dates
1.	Port Hueneme (Navy)	02/94
2.	McClellan AFB (Air Force)	03/94
3.	Wurtsmith AFB	11/94
4.	VAAP (Army)	11/94
5.	Controlled Release Site	07/95
6.	Navy #2/Army #3 POL/Heavy Metal Location	07/95
7.	Army Location #2	09/95
8.	Navy Location #3	05/96

10. Transition Plan:

Cost and performance data will be collected by the standardized methodology. At the conclusion of the demonstrations, summary sheets will provide a brief analysis and these will be followed by technical reports documenting the demonstrations. These steps will lead to the fabrication and procurement guidance that will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement the technology

acceptance. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	FY01	TOTAL
Air Force	3100	2850	1450	1350	1350	1450	1450	1450	14450
Army	2370	2120	2120	2120	1900	1500	1000	1000	14130
Navy	650	1450	900	900	600	600	600	400	6100
EPA	2100	6500	3300	3500	3500	1000	1000	1000	21900
TOTAL	8220	12920	7770	7870	7850	4550	4050	3850	56580

12. Performers:

Performers include the U.S. Air Force, the U.S. Army, the U.S. Navy, USDOE, and the USEPA. Other principal partners in this initiative will be other federal agencies and the private sector. The SERDP Executive Director and the Deputy Undersecretary of Defense for Environmental Security will provide program oversight. On site execution and day-to-day oversight will be performed by private firm contractors and/or government agencies.

13. Principal Investigators:

Major Mark H. Smith, PhD
AL/EQW
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
(904) 283-6290

Mr. Eric Koglin
U.S. EPA EMSL-LV
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2432

Mr. Theodore Ruff
USAEC
SFIM-AEC-TSD
APG, MD 21010-5401
(410) 671-1560

Mr. Ernest Lory
NFESC, ESC-411
560 Center Dr.
Port Hueneme, CA 93034-4328
(805) 982-1299

Walter J. Weber, Jr. Ph.D.
101 EWRE Building
The University of Michigan
Ann Arbor, MI 48109-2125
(313) 763-2274

14. Keywords:

Bioremediation; Technology demonstrations (remediation); DNAPL (dense nonaqueous phase liquid); Explosives; Petroleum, Oils, and Lubricants (POL); Solvents; Technology Transfer; Hazardous Waste Site Characterization; Measurement and Monitoring Technologies.

At the time of printing, a detailed project description had not been received for:

Northeast Institute for Environmental Remediation

TABLE A-II FY 1994 COMPLIANCE PROJECTS	Funding $(K) FY94	ID Number	Page Number
Boiler/Engine Emissions			
Metal Perovskite Catalysts for NOx Reduction (AF)	175	177	A-158
Steady-State/Nonsteady-State NOx Emission Control (AF)	850	183	A-162
e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-Products (DNA)	2,600	82	A-165
Compact, Closed-Loop Controlled Waste Incineration (N)	1,000	34	A-169
Reduction of NOx Emissions from Marine Power Plants (N)	750	42	A-174
General Hazardous Waste Management			
Lead-Based Paint Hazard Mitigation (A)	700	521	A-179
Emission Reduction Planning Model (AF)	200	175	A-184
Laser Ablation/Ionization Characterization of Solids (DOE)	380	362	A-188
Vapor Permeation VOC Recovery from Refueling and Storage (EPA)	250	252	A-192
Solid Waste Encapsulation (DOE) *	100	820	A-195
Monitoring			
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)	500	192	A-196
Leak Location in Underground Pipelines (EPA)	1,000	249	A-201
Air Quality Monitor (AF) *	350	821	A-206
Noise Impacts			
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)	550	523	A-207

TABLE A-II FY 1994 COMPLIANCE PROJECTS	Funding $(K) FY94	ID Number	Page Number
Open Burning/Open Detonation			
Characterization Open Burning/Open Detonation Emissions (A)	1,128	247	A-212
Measuring and Modeling for OB/OD Permitting (EPA)	350	251	A-217
Physical Treatment Processes			
Hydrothermal Reduction of Energetic Wastes (AF)	375	180	A-221
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	380	315	A-225
Kinetics of Supercritical Water Oxidation (DOE)	740	364	A-230
Photocatalytic Process to Treat Pink Water-2 (DOE)	0	349	A-235
Waste Forms Based on Separations Media (DOE)	200	360	A-240
Supercritical Water Oxidation of Organic Wastes (N)	364	35	A-245
Shipboard Emissions			
Shipboard Non-Oily Wastewater Treatment System (N)	400	29	A-249
Waste Minimization/Recycling			
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A)	800	524	A-253
Other			
National Environmental Education and Training Center (A) *	3,500	819	A-257
Compliance Total	17,642		

* Congressional Interest

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Metal Perovskite Catalysts for NO_x Reduction

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Lab

5. **Proposal ID:** #177

6. **Problem Statement:**

Goal: The goal of this research is to investigate whether oxygen deficient strontium-lanthanum cobaltate ($Sr_xLa_{1-x}CoO_3$) can be stabilized for long-term use as a catalyst for reduction of oxides of nitrogen (NO_x).

Background: The control of NO_x emissions is mandated by federal, state, and local regulations. These sources are generally characterized by high-temperature combustion of fossil fuels, where organically bound nitrogen in the fuel oxidizes to form NO and small amounts of NO_2 and N_2. (In most cases, NO_2 emissions will be as low as 5-10 percent by volume of total NO_x emissions.) While fuel combustion to produce commercial power and motor vehicle emissions are the two largest contributors in the United States to NO_x production, other sources have been targeted as well, including jet engine test cells (JETCs). Existing methods to remove NO_x from combustion exhausts do so only under a narrow range of conditions.

Previous investigations have shown that NO can be reduced by levels greater than 90 percent by $LaCoO_3$ catalysts. Conversion of NO increases from less than 10 percent at temperatures below about 450°C to over 90 percent at about 525°C for internal combustion engine exhausts with air-to-fuel ratio of 12.85. At 660°C, an air-to-fuel ratio of 14.35 resulted in 90 percent conversion of NO (excess air requires higher conversion temperatures). Stability can be expected at relatively higher temperatures, as $LaCoO_3$ has a melting point of 1607°C, and the La--Co--O system has a low temperature eutectic in air at 1482°C. The presence of CO in exhaust air enhances the conversion of NO while O_2 reduces NO conversion. CO reacts with H_2O and produces H_2, which at sufficiently high temperatures, acts to reduce the $LaCoO_3$ catalyst, resulting in an oxygen deficient structure. This oxygen vacancy allows for chemisorption of CO or NO, and likewise acceleration of the conversion reaction of NO and CO to N_2 and CO_2. As the conversion process continues, the $LaCoO_3$ is reduced through a complex series of reactions, which are accelerated in the presence of O_2. At weight losses above 3.5 percent, phase changes begin to occur and Co metal is formed, resulting in loss of catalytic activity. The addition of an Sr ion by replacing one La ion (yielding $Sr_xLa_{1-x}CoO_3$) may result in a faster and lower temperature conversion of NO, while withstanding higher levels of reduction before losing effectiveness as a catalyst. Previous investigations suggest that the $Sr_xLa_{1-x}CoO_3$ catalyst can withstand weight losses of between 8-9 percent before reverting to Co metal. Concentrations of selected species (such as oxygen) during reactions can be monitored using electrochemical cells. By controlling the oxygen concentrations, the reduction of the catalyst can be controlled.

7. Project Description:

Technical Objective: The technical objective of this project is to investigate the thermodynamics and kinetics of reduction of $Sr_xLa_{1-x}CoO_3$ in NO and determine the limits of stability of the active oxygen deficient phase to establish the effectiveness of $Sr_xLa_{1-x}CoO_3$ for use as a long-term NO_x catalyst. Representative NO environments containing gases which can be expected in exhaust streams of interest (e.g., JETCs) will be used.

Technical Approach: All basic research for this project will be on the laboratory scale, including modeling of representative exhaust streams. (1) The thermodynamics and kinetics of reduction of $Sr_xLa_{1-x}CoO_3$ will be analyzed using techniques involving thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and the use of high-temperature electrochemical cells to measure oxygen activity. X-ray diffraction techniques will be used for crystallographic examinations. Models for thermodynamic and kinetics of phase equilibria of the oxygen deficient phase will be developed. (2) Developing techniques for stabilizing the oxygen deficient phase will involve investigating effects of varying stoichiometry on stability of the ceramic material and examining the feasibility of using solid state electrolytes (YSZ) to control the extent of reduction of the catalyst. Once a technique to stabilize the active phase has been developed, the kinetics of conversion of NO will be investigated to determine efficiency and speed of catalysis of NO. (3) Models of the catalysis of NO by $Sr_xLa_{1-x}CoO_3$ will be developed and reported.

Technology demonstration will be performed at an Air Force facility. Tyndall AFB FL and McClellan AFB CA are potential candidates. (1) Technical data required for installation of the slipstream and full-scale emission control systems will be gathered. Prior experience and information gained from related projects will be beneficial in completing this task. (2) A sub-scale system will be designed and installed to evaluate performance of the catalyst under near-full scale operating conditions. A multigas analyzer in conjunction with a computer data acquisition system will be utilized to provide continuous emissions monitoring during testing. (3) Results from the sub-scale prototype system will be evaluated and reported. These results will be used in the design of a full-scale prototype control system for a JETC. (4) The control system will remain in use for a sufficient time to determine the long-term stability and life cycle of the catalysts. The same data acquisition system will be utilized. (5) Test results will be evaluated and reported.

Relationship to DoD Environmental Objectives: This research, as applied to DoD JETCs, directly contributes to the requirement to control maintenance process emissions as identified in the Tri-Service Environmental R&D Strategic Plan, DoD Pillar 2: COMPLIANCE; Requirement Thrust 2.B.2: Maintenance Process Emissions (Test Stands and Cells).

Relationship to Other Work: This is an alternative approach applicable to NO_x removal from JETCs. A Small Business Innovative Research (SBIR) program initiated seven independent approaches to NO_x control for JETCs and identified one, a vermiculite--MgO sorbent process, as the most practical and cost-effective at present state of development. Promising technologies such as the $Sr_xLa_{1-x}CoO_3$ catalyst should be pursued as a potential marketable NO_x reducer and replacement NO_x control for JETCs in the event the vermiculite--MgO sorbent fails as a practical control device.

Technical Risks: There are some limited risks in this research. It may be difficult to control the degree of reduction of the catalyst, precluding long-term use. In addition, the catalytic activity

of strontium-doped lanthanum cobaltate may be too slow to act as a fast catalyst needed for current applications.

8. Expected Payoff:

Potential Users: Air Force major command operations and maintenance activities that emit combustion exhausts, other DoD operations and maintenance activities, and private operations could benefit from this research.

Impact: If successful, this work can lead to effective and inexpensive catalysts for NO and CO conversion. The catalyst has the potential to benefit many applications with high-temperature NO_x reduction, including JETC emission controls, and possibly direct emissions from jet engines and combustion sources. $Sr_xLa_{1-x}CoO_3$ has a relatively low concentration of strategic materials and applications where $Sr_xLa_{1-x}CoO_3$ could replace platinum may be identified.

9. Milestones:

Phase I		
1.	Materials Preparation	09/94
2.	Design and Construction of Testing Apparatuses	12/94
3.	Investigate Thermodynamics and Kinetics of Reduction of Oxygen Deficient Phase	09/95
4.	Phase I Final Report	10/95
Phase II		
5.	Identify Techniques to Stabilize the Oxygen Deficient Structure	03/96
6.	Investigate the Kinetics of NO Reduction by Stabilized $Sr_xLa_{1-x}CoO_3$	09/96
7.	Phase II Final Report	10/96
Phase III		
8.	Complete Investigations and Development of Models	09/97
9.	Final Report	10/97

Demonstration Phase

Phase I		
1.	Define Test Cell System Requirements	09/97
2.	Design and Fabricate Prototype Apparatus	12/98
3.	Slipstream NO Reduction Tests	06/98
4.	Evaluate Test Results	08/98
5.	Phase I Final Report	09/98
Phase II		
6.	Design, Fabricate, and Install Full-Scale Prototype System	12/98
7.	Full-Scale NO Reduction Tests	09/99
8.	Evaluate Test Results	12/99
9.	Phase II Final Report	01/00
Phase III		
10.	Technology Transfer	03/00

10. Transition Plan:

The results of the 6.2 basic research will be used in a follow-on 6.3 technology demonstration effort where catalyst performance in controlling emissions from an operational JETC will be demonstrated at an Air Force facility. Favorable results would allow technology transfer to the Environmental Systems Program Office (HSC/YA) for EMD and fielding. Technical reports and articles will also be produced for the R&D community, other agencies, and industry.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	Total
SERDP	175	100	90	450	350	350	1515

12. Performers:

This is a joint research effort between: Air Force Armstrong Laboratory Environics Directorate, Environmental Compliance Division (AL/EQS); and Army Construction Engineering Research Laboratories (USACERL). Research will be conducted in-house by USACERL and field-demonstrated at an Air Force facility.

13. Principal Investigators:

AIR FORCE
Dr. Joseph D. Wander
AL/EQS
139 Barnes Dr., Suite 2
Tyndall AFB, FL 32402-5323
TEL: (904) 283-6240
FAX: (904) 283-6286

ARMY
Dr. Ellen G. Segan
US Army CERL
PO Box 9005
Champaign IL 61826-9005
TEL: (217) 373-6768
FAX: (217) 373-7222

14. Keywords:

Perovskite, NO_x, Air pollution, Catalyst, Doping, Cintering.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Steady-State/Nonsteady-State NOx Emission Control

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Laboratory

5. **Proposal ID:** #183

6. **Problem Statement:**

Limitations of mass transfer cause combustion processes to be imperfect, and to produce such polluting byproducts as oxides of nitrogen (NOx), soot, and incompletely oxidized hydrocarbons. Whereas the effects of NOx in the high atmosphere are presently a matter of speculation, NOx has been identified as a significant contributor to the formation of ozone in the low atmosphere. Stationary sources of NOx are or will shortly be regulated under provisions of the Clean Air Act Amendments (CAAA) of 1990. Fair methods of control are available for stationary sources operating at or near steady state, but none have been demonstrated for jet engine test cells (JETCs), which operate at transient conditions that vary drastically during operation. The next target for regulation is mobile sources, which emit much larger quantities of pollutants than do stationary operations.

7. **Project Description:**

Results from phase 1 and 2 Small Business Innovation Research (SBIR) contracts determined that magnesia coated on vermiculite (MgO-V) and activated carbon (C) capture NOx from simulated and actual combustion exhaust gases at temperatures below 300°F and release them at temperatures above 250°F. Installation of a prototype control device on a JETC testing subscale drone jet engines determined that about 65% of NOx, soot, and carbon monoxide (CO) is removed during passage of the exhaust gas through an 8-inch bed of MgO-V, preceded by a 4-inch bed of untreated vermiculite or C. However, back pressure was a significant problem, requiring that much of the exhaust stream bypass the beds to decrease average flow resistance. This project will (1) build and install an engineering test facility on an operating JETC at McClellan AFB CA, which will be used to tune the sorbent beds and supporting air-moving hardware to provide the best attainable control at a back pressure that is tolerable to the most-sensitive new-generation engines. This will be the definitive determination of the practicability of controlling JETC emissions directly, and it will include a determination of the economics of applying such a control device; (2) assemble a prototype control device utilizing the same chemical principle and apply it to three stationary, near-steady-state sources (an incinerator, a bank of diesel power generating units, and a space heater in a paint-curing facility the field incinerator in the original proposal was not permitted for use] to measure efficiency and cost of control; (3) assemble a prototype control device and perform in-lab and on-the-road testing on exhausts from a gasoline-powered automobile and a diesel truck.

8. Expected Payoff:

Each of the applications is effectively independent of all of the others, so each may succeed independent of the outcome of the other experiments. The JETC control will either provide a practical control technology allowing economically feasible decontamination of engine exhausts during test operation, or it will determine that control of JETC emissions is impractical and that the only available modes for regulation of JETCs are permitting and meteorological constraints. For the stationary and mobile near-steady-state sources, the payoffs are a quantitative improvement in pollutant removal, a decrease in the cost and effort to maintain the control devices, wider operating windows for temperature and throughput, and avoidance of the liability of storing, handling, and possibly leaking hazardous materials used in selective reduction methods. For all applications, the treatment residue is nonhazardous and beneficial to plants, allowing horticultural disposition, and avoiding the cost of disposal of process-derived hazardous wastes.

9. Milestones:

1.	Date of Award	03/94
2.	Regeneration Method for Used Sorbents	09/94
3.	Design of Prototype (Generator, Vehicles, Gas Burner, Test Cell)	10/94
4.	Prototype Construction (Generator, Vehicles, Gas Burner)	12/94
5.	Prototype Installation (Vehicles, Gas Burner)	12/94
6.	Prototype Installation (Generator)	01/95
7.	Prototype Construction (Test Cell)	01/95
8.	Characterization of Removal Chemistry and Transport Phenomena	03/95
9.	Prototype Installation (Test Cell)	03/95
10.	Completion of Testing (Vehicles, Gas Burner)	05/95
11.	Prototype Design (Incinerator)	05/95
12.	Prototype Installation (Test Cell)	05/95
13.	Completion of Testing (Generator)	06/95
14.	Prototype Installation (Incinerator)	10/95
15.	Completion of Testing (Incinerator)	02/96
16.	Completion of Testing (Test Cell)	03/96
17.	Completion of Landfill and Byproduct Evaluations	03/96
18.	Completion of Cost Analyses	03/96
19.	Final Reports Accepted	06/96

10. Transition Plan:

The test cell control system will effectively transition itself. EPA's regulatory group is unable to dictate controls for test cells because no technology has been demonstrated. For situations to which this technology is practically applicable, EPA will specify this control as maximum available control technology. The other stationary and mobile source controls will be complete packages is marketable form, ready for delivery through commercial channels or for licensing. The test cell prototype will remain in use at the conclusion of this effort, and the other prototypes may be left in operation, at the discretion of McClellan AFB personnel.

11. Funding: ($K)

	FY94	FY95	TOTAL
SERDP	850	850	1850

12. Performers:

The Environics Directorate of Armstrong Laboratory (AL/EQS), Tyndall AFB FL, POC; Sorbent Technologies Corporation, performing contractor; SMALC/EMPV/LARD, McClellan AFB CA, site personnel supporting installation and testing. Anticipate EPA Air and Energy Engineering Laboratory participation during data collection and analysis.

13. Principal Investigator:

Dr. Joseph D. Wander
AL/EQS
139 Barnes Dr., Suite 2
Tyndall AFB, FL 32402-5323
TEL: (904) 283-6240
FAX: (904) 283-6286

14. Keywords:

NOx, Nitrogen Oxides, Combustion, Vermiculite, Air Pollution, Sorbent.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-products

3. **Agency:** Defense Nuclear Agency (DNA)

4. **Laboratory:** DNA e-SCRUB Facility, Alexandria, Virginia

5. **Proposal ID:** #082

6. **Problem Statement:**

The goal of the e-SCRUB program is to demonstrate that the High Power Transformer Accelerator (HPTA) technology, originally developed for military applications, can be applied to environmental compliance. This goal includes the integration of the HPTA technology into the electron beam dry scrubbing (EBDS) process to demonstrate a cost effective process for removing:

SO_2 and NOx from flue gas emitted from boilers burning high sulfur fuel

SO_2, NOx, and air toxins from incinerators burning municipal solid waste

The Clean Air Act Amendment for 1990 (CAAA) mandates significant reduction from present levels of SO_2 and NOx from utility boilers and SO_2 and NOx, and air toxins emitted from incinerators burning municipal solid waste (MSW).

Current state-of-the-art technology such as limestone scrubbing for de-SOx and selective catalytic reduction (SCR) for de-NO_x from boilers burning low sulfur fuel. However, these technologies are not cost effective for simultaneously removing SO_2 and NOx from high sulfur (i.e., greater than 2,000 ppm) fuel and SO_2, NOx, and air toxins from incinerators burning MSW. Thus, in order to comply with CAAA, utilities burning high sulfur fuel will have to change to an alternate type of fuel, which will cause a devastating economic impact on the producers of high sulfur fuel.

Until now, conventional electron beam generators have been too expensive and insufficiently reliable for cost effective application of electron beam dry scrubbing (EBDS). However, in support of nuclear weapons effects simulation (NES), the Balanced Technology Initiative (BTI), and the Ballistic Missile Defense Office (BMDO), DNA has developed electron beam generator technology using HPTA technology. This can potentially satisfy the power (0.5 to 2 MW per module), size (40 m^3 per 2 MW module), and cost ($2.40 per beam watt) requirements for an affordable EBDS process for civilian utilities and DoD boilers burning high sulfur coal and incinerators burning MSW.

Successful implementation of e-SCRUB will allow the continued use of high sulfur coal in compliance with the CAAA, while avoiding the adverse economic impact in high sulfur coal producing areas such as Appalachia.

In addition, the demonstration of a cost effective high average power electron beam generator can be used for the neutralization and destruction of volatile organic compounds and pathogens found in gaseous, aqueous, and solid waste streams. These include the cleanup of the so called "red and pink water" resulting from the processing of explosives, and treatment of sludge and sediments, including hazardous mixed wastes with heavy metals.

The Phase 1 program began Jan 93 and is planned to be completed by Jan 95. In Phase 1 we will demonstrate that the cost and size objectives for the electron beam generator are met ($2.40 per beam watt and 40 m^3 per 2 MW generator), which are one-third and one-fourth of current technology. The major elements and support system of the electron beam generator already fabricated under the Phase 1 (FY 92 funding) effort are:

a. Slow power conditioning (SPC) system, which includes the main power supply, command resonance charge unit, and the thyratron switch unit;

b. Saturable reactor modulator, which includes saturable reactor units, pulse forming lines, output lines, and reset circuits;

c. High power transformer accelerator (HPTA), which includes 24 Metglas cells, HPTA support structure, and cathode stalk and support structure;

d. Instrumentation, control, and diagnostics, which includes all electronics for monitoring, safety interlocks, operation, and fault analysis;

e. A complete government test facility, which includes oil, water, and vacuum subsystems, heat exchangers, flowing gas load (duct-work, dryers, and blowers), installation of 2.5 MW prime power, conduits, storage tanks, and thermal management subsystems.

In addition to the hardware development outlined above, other Phase 1 achievements completed with the FY92 SERDP funds include benchmarking the multi-zone irradiation zone EBDS process for the high sulfur conditions associated with US high sulfur coal. This work was done by the Karlsruhe Nuclear Research Center in Germany (KFK). Furthermore, in response to the SERDP Scientific Advisory Board (SAB) directive given at the SAB review, an initial survey of potential civilian utility sites was undertaken and the economic value of by-products as a fertilizer feed stock was investigated and established by West Virginia University.

7. Project Description:

The Phase 2 effort uses FY93 and FY94 funding. The period of performance is 12 months.

The purpose of the Phase 2 program is to build upon and significantly extend the results of both the pulsed power efforts and further developments of the EBDS process. As discussed above, the Phase 1 program has met the cost and size objectives for the electron beam generator equipment. The major risk is reliability. In order to reduce this risk, the pulsed power conditioning subsystems will be tested extensively at the 0.5 MW, and effectively the 2 MW levels in order to establish the mean-time-between-failure (MTBF) and system reliability.

In addition, the process results at KFK will be extended and verified at a pilot plant scale (20,000 m^3 per hour). Also, a cost effective and reliable by-product collection device that is

manufactured by a US vendor will be demonstrated at the facility, along with an approach that demonstrates anode reliability in the presence of the flue gas.

A Phase 3 demonstration plant capable of processing 200,000 m^3 per hour will be selected. The treatment facility design will be completed in sufficient detail to allow its construction immediately at the start of Phase 3. Furthermore, a plan will be initiated for achieving the transfer of the technology to industry after Phase 3.

Finally, the groundwork, will be laid in Phase 2 for alternative applications of the e-SCRUB technology. These include scrubbing of flue gas from incinerators burning MSW, electron beam purification of drinking water, treatment of wastewater, treatment of gaseous, aqueous, and solid waste streams contaminated with various toxins such as volatile organic compounds (VOCs) (specifically to include "red and pink water").

8. Expected Payoff:

The expected payoffs for the e-SCRUB program are:

a. Demonstration of a cost effective approach for removing SO^2, NOx, and air toxins from coal fired boilers and MSP incinerators.

b. Technology transfer to civilian utilities which use high sulfur content coal can with CAAA. Thus, the program will avoid the devastating economic impact of the CAAA on producers of high sulfur content coal.

c. Allow the cost effective application of electron treatment for a variety of environmental application such as purification of drinking water, cleanup of contaminants from gaseous, aqueous, and solid waste steams.

9. Milestones:

Phase 1: Jan 93-Jan 95:	Meet cost and size goals Demonstrate continuous operation: Jan 95

Program Review Prior to Phase 2 Start:

Phase 2: Feb 95-Sep 96:	Establish scalability and reliability: Operate 1 MW generator under 2 MW conditions; select site for Phase 3 Demonstration; conduct initial alternative applications analysis and experiments
Phase 3: Jan 96-Jun 97:	Conduct utility plant demonstration; conduct small scale alternative applications; optimize electron beam generator for further cost, size, efficiency, and reliability improvements

10. Transition Plan:

After completion of all three phases of the SERDP program, we will have assembled an industrial team that will proceed with the commercialization of e-SCRUB. Beginning with the Phase 2 effort, we will demonstrate the ability to transfer this technology to the utility industry. Furthermore, we will require that the prime contractor create a business plan so that the electron beam equipment can be supplied to the utility industry and for other environmental applications.

11. Funding: ($K)

We request a total of $2,600,000 of FY94 SERDP funds. These funds will be used to complete Phase 1 objectives and to begin the Phase 2 effort once the Phase 1 objectives are fully satisfied.

First release of funds:
Phase 1 Completion: $1,000 Assembly & Test of Electron Gun
300 Facility Fixed Costs
Second release of funds after meeting Phase 1 goal and SAB review:
Phase 2 Start: $ 500 Assembly & Checkout of Second 500KW Modules
800 1MW Reliability Testing to 1000 hours
Total FY94 Request $2,600

	FY94	FY95	FY96	TOTAL
Phase 1	1,300	0	0	1,300
Phase 2	1,300	5,000	2,700	9,000
Phase 3	0	4,000	8,000	12,000
TOTAL	2,600	9,000	10,700	22,300

12. Performers:

The government program manager is the Defense Nuclear Agency (DNA) with policy and oversight from the Deputy Under Secretary of Defense for Environmental Security.

13. Principal Investigators:

Major Jeffrey Cukr
Defense Nuclear Agency, RAST
6801 Telegraph Rd
Alexandria, VA 22310
Phone: 703-325-0905
FAX: 703-325-2959

Mr. James Marsh
Assistant Deputy Under Secretary of Defense
for Environmental Technology
Rm 3E787, Pentagon
Washington DC 20301
Phone: 703-697-9106

14. Keywords:

electron beam dry scrubbing, flue gas scrubbing, high power electron beam generator

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Compact, Closed-Loop Controlled Waste Incinerator

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Weapons Division China Lake, CA 93555-6000

5. **Proposal ID:** #034

6. **Problem Statement:**

A new generation of incinerators based on recently developed active ramjet-combustion control is required for ship-board waste disposal to enable Navy ship access to ports and bodies of water around the world without operational constraints from environmental laws and regulations. The present practice of over-board discharge and storage/off-loading becomes unacceptable. Thermal destruction is considered the ultimate solution beyond 2000 for all types of waste, including trash, garbage, plastics, medical and hazardous wastes. The need for improved waste disposal is clearly identified in the Tri-Service Environmental Quality R&D Strategic Plan as shown later. Present commercial incinerators are typically unsuitable for Navy shipboard installation and operation because they are oversized and often do not meet incineration standards, in particular at off-design operation. Oversizing in the present system, in terms of air and auxiliary fuel mass flows, reactor size, and air pollution control system is necessary because physical understanding of interrelated processes in mixing and combustion is limited and control authority over the various steps which make-up the incineration process does not exist.

For ship-board use, compact (small size) incinerators with assured (pollution-free) waste destruction during design and off-design operation are essential. Potential development of these advanced incinerators is made possible through recent accomplishments in combustion control which is based on the detailed understanding of acoustic/fluid dynamic/combustion interactions. This new understanding was in part developed under ONR sponsorship to improve ramjet performance. When applied to waste incineration, improved waste destruction efficiency was demonstrated in preliminary tests with controlled pressure oscillations for improved heat transfer using solid waste and for establishing organized vortical structures for controlled incineration using gaseous and potentially liquid waste. In particular, the use of active control to maintain optimum conditions between pressure oscillations, vortical structures and waste/fuel injection was effective and emerged as a promising feature for advanced incinerators. For active combustion control, novel sensors are continuously monitoring in real-time the combustion process and the exhaust, and are actively manipulating the important steps of the incineration process via a controller and actuators. Further improvements can be expected from closed-loop active control.

Based on the above results, the ONR research program "Combustion Control in Compact Waste Incinerators" within the Environmentally Sound Ship Program was started in late FY93. This collaborative research program between NAWCWPNS and three universities is aimed to provide scientific insight for the demonstration of a compact incinerator with Dr. Klaus Schadow, NAWCWPNS, on detail to ONR as program coordinator. Future funding originally planned for

this research program has been absorbed into the SERDP program. This present SERDP proposal will (1) provide continued funding of the basic research program started at ONR, (2) expand current basic research efforts to include novel sensor research, (3) start applied research in actuator and sensor technology, and (4) initiate transition of the research to demonstrate assured (pollution-free) incineration in a compact prototype device for ship-board use. Technology transfer will be an important part of the proposal. Several companies including APV Chemical Machinery, Hypertat Corporation, Energy and Environmental Research Corporation, and SonoTech Inc., have expressed interest in applying the new technology of compact incinerators to the civilian sector. Compact incinerators will allow disposal of the waste on the same site where it is generated, without need for waste transportation. This is of particular importance for medical waste.

7. Project Description:

The overall goal of the proposal is the demonstration of a compact prototype incinerator with closed-loop active combustion control. This new approach for achieving assured (pollution-free) waste destruction in a compact system requires the physical understanding of the various steps in the incineration process, and the use of appropriate sensors and actuators. The project consists of four concurrent tasks of basic and applied research, and incinerator prototype demonstration:

(1) The physical understanding for active combustion control is presently extended to waste incineration in the above mentioned ONR program. It is proposed to continue this basic research under SERDP funding to control the mechanisms of pyrolysis, gasification, combustion and pollution in the core of acoustically driven vortical structures and define mechanisms of the recently observed increases in solid waste incineration efficiencies in the presence of resonant acoustics. In particular, closed-loop active control will be studied.

(2) With the new physical understanding, control authority on the incineration process will be established. To implement active, closed-loop control, sensors for real-time, continuous exhaust monitoring are required which provide the input to the actuators to maintain desired pressure oscillations and modulate auxiliary air/fuel and waste injection. It is proposed to expand the basic research to explore new laser-based diagnostics. Surrogate species will be used as a performance indicator as also proposed for compliance with the Clean Air Act. There are a number of potential optical techniques for real-time sensing of target species, which include Broadband Infrared Absorption/Emission, Laser-Induced Fluorescence, Fourier Transform Infrared Spectroscopy, and Tunable Diode-Laser Spectroscopy.

(3) Concurrent with the basic research, an applied research program will be initiated to develop sensors and actuators for combustion control. Research and development work is required for sensors to monitor critical combustion steps, for acoustic actuators to maintain desired resonant pressure oscillations, and for mass-flow actuators to modulate gaseous and liquid flows at high frequencies.

(4) The basic and applied research provides the foundation for the demonstration of a closed-loop controlled compact incinerator. One concept of a solid waste incinerator consist of a combination of a primary and secondary chamber. In the primary chamber (for example rotary kiln), controlled pressure oscillations will be used for improved heat transfer and waste decomposition/combustion; in the secondary chamber, complete waste combustion (afterburning) is obtained with synchronized air/fuel injection into acoustically driven vortices.

Output from emission sensors will be used as control input. In another concept for hazardous gaseous and liquid wastes, waste combustion in the core of vortices with synchronized waste/fuel injection using closed-loop active control will be demonstrated.

The proposed advanced incinerator solution addresses many requirements of the Tri-Service Environmental Quality R&D Strategic Plan (for example 2.L.1.-2.III.1.b.; 2.L.7.-2.III.3.b.; and 2.I-2.III.1.f.) listed under Pillar II (Compliance), which involves waste treatment and disposal. The proposed demonstration of a compact incinerator with assured destruction is of immediate need to the Navy for ship-board use, but also for off-shore use by the Navy, Army, Air Force, and DOE for on-site waste destruction.

8. Expected Payoff:

Successful demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represent a significant step towards assured waste incineration. The type of system proposed here has the potential for ship-board applications, and will be essential to the development of environmentaliy sound ships beyond 2000. Compact incinerators are also desirable for on-shore use in the government and private sector. Small, compact incinerators will allow on-site waste destruction and avoid waste transportation to large incineration sites. In particular, medical waste incineration is a prime candidate in the private sector for a compact system. The closed-loop active control of the incineration process will for the first time assure proper operation during design and off-design operation. Successful demonstration of the assured waste incineration on-board ships will result in significant cost savings by avoiding cost, for waste off-loading and on-shore destruction, in particular in foreign countries.

9. Milestones:

The following milestone schedule for the four tasks assume funding will be on board 6/94.

Combustion control research (6.1)

1.	Determine critical incineration processes for active control	9/94
2.	Provide concept/design input for all other tasks	3/95
3.	Provide specifications for sensor research and actuator R&D work	6/94
4.	Complete basic active control research and provide input for incinerator demonstration	9/95
5.	Complete active control with different waste surrogate types and provide input for incinerator demonstration	9/96

Sensor Research (6.1)

1.	Complete review of possible scientific approaches	9/94
2.	Provide concept/design input for sensor R&D program	3/95
3.	Complete laboratory evaluation of a prototype sensor and provide input to sensor R&D program	9/95
4.	Complete evaluation of additional sensors in a lab and hostile environment	9/96

Sensor and Actuator R&D Program (6.2)

1.	Complete review of possible actuator technologies	9/94
2.	Provide concept/design input of actuator for compact-incinerator demonstration	3/95

3. Complete design and fabrication of actuator/input to demo program 9/95
4. Complete laboratory evaluation of sensor and provide input for incinerator demonstration 3/96
5. Complete system evaluation of various sensors and actuators and provide input for incinerator demonstration 3/97

Incinerator demonstration
1. Select industrial partner 9/94
2. Complete design of incinerator concept 6/95
3. Complete exploratory incinerator tests 6/96
4. Complete preliminary incinerator evaluation against incineration standards and regulations 3/99
5. Complete evaluation of optimized incinerator 9/97

10. Transition Plan:

At the beginning of the incinerator demonstration program, negotiations of technology transfer agreements (CRADA) will be initiated. Potential partners are Inerson, Simonds, and Consumat. These companies are prime candidates with manufacturing experience in small medical and municipal waste incinerators. In addition, a Small Business Innovation Research (SBIR) request for the demonstration of a compact, closed-loop controlled waste incineration has been submitted in September 1993. Also, additional funding sources for the incineration demonstration program will be explored, including the Gas Research Institute, the American Plastics Council and the Medical Industry Council.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	Total
SERDP	1000	1400	1500	1200	5100

12. Performers:

The active control research described earlier is a collaboration between Georgia Institute of Technology, University of Colorado, Boulder, University of California, Los Angeles, and the Naval Air Warfare Center Weapons Division, China Lake, CA, with Dr. Klaus Schadow, NAWCWPNS/ONR (on detail), as program coordinator. The sensor research will be performed at Sandia National Laboratory, Livermore, CA,in collaboration with a yet to be determine university with Dr. Jay Keller, SNL, as program coordinator. The sensor and actuator R&D program and the integrated prototype incinerator demonstrator will be done by NAWCWPNS and SNL in collaboration with industrial partners. Prime candidate is Environmental Research Corporation (Dr. Seeker). This company is presently evaluating a different integrated prototype waste demonstrator for DOE. They have expressed strong interest in the compact, actively controlled waste incinerator. Dr. Klaus Schadow will be program coordinator of the sensor and actuator program, as well as the incinerator demonstration program.

13. Principal Investigator:

Dr. Klaus C. Schadow
Head, Propulsion Research Branch
Naval Air Warfare Center Weapons Division, Code C02392
China Lake, CA 93555
TEL: (619) 939-6532
FAX: (619) 939-6569

14. Keywords:

Incineration, compact design, active combustion control, real-time monitoring, closed-loop control, acoustic/fluid dynamic/combustion interactions

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Reduction of NO_x Emissions from Gas-Turbine Power Plants

3. **Agency:** U.S. Navy, Naval Surface Warfare Center, Carderock Division

4. **Laboratory:** Annapolis Detachment, Machinery R&D Directorate

5. **Proposal ID:** #042

6. **Problem Statement:**

The California Air Resources Board (CARB) and the Environmental Protection Agency (EPA) are expected to mandate limitations on the emissions of NO_x from ships passing through or operating within 100 nautical miles of the United States littoral by CY1995. Consequently, the Navy has been directed by OPNAVINST 5090.1A to make a good-faith attempt to comply with these limits on emissions in order to avoid costly fines and litigation.

At least 131 destroyer and frigate class ships employ gas-turbines plants, the LM2500, for propulsion, and many more also use the 501K gas turbine for power generation, representing an all-ship inventory of about 700 turbine units. These ships, returning periodically from remote tactical duty stations to replenish resources at home ports, pass through coastal waters within the 100-mile limit. The emissions from their power plants are presently in severe violation of the proposed NO_x limits for gas turbines.

Current state-of-the-art developments in low-emissions gas turbines are based on a dry low NO_x (DLN) combustor, and a water-injected low-NO_x combustor (which is similar in some aspects to the steam-injected combustor of General Electric's steam-injected gas turbine). Both are capable of reducing NO_x emissions below the anticipated CARB-mandated 42 volume ppm limit for gas turbines. Both combustors rely on a decrease in the average temperature of the flame zone to reduce the production of NO_x. (High temperature catalyzes the cleavage of the nitrogen molecule.) However, to cool the flame zone by air dilution, the size of the DLN combustor must increase substantially. To cool the flame zone with water, purified water normally available from the ship distillation plant, is required.

It is anticipated that for new construction, of the two technologies, the DLN combustor will have the least ship impact and cost. Nevertheless, the DLN spatial requirements reflect some uncertainty over whether the DLN system is subject to immediate retrofit without some rearrangement within the existing unmodified LM2500 enclosure. Modification of the component configuration within the enclosure. Modification to the component configuration within the enclosure to provide compatibility with the geometry and spatial requirements of the DLN combustor appears necessary. Based upon the fact that the General Electric Company already markets, for NO_x suppression in the existing engine, a water-free manifold, the water-injected combustor (WIC) represents an inexpensive, low-risk, alternative system, which is immediately amenable to retrofit in the LM2500 enclosure. Even if no problems are encountered in the DLN modifications, demonstration of a WIC system for NO_x reduction represents a prudent fallback development of a proven (in land-based plants), simpler, retrofit system.

Guiding principles expounded above for gas turbines are not universally applicable to diesel engines. For example, the DLN combustor approach would not be employed. Of the combustion-flame-cooling methods, water injection has been examined by many researchers in the academic and/or diesel contractor community with positive expectations that WIC methods may satisfy Navy needs for abatement of emissions in diesel plants. However, there will be a different retrofit response for ocean-going (such as the LST41 and some LCD-class ships) as opposed to harbor craft. Although the emission levels of diesels are much greater than the emissions of gas turbines (as high as 2300 ppm compared with 400 ppm for gas turbines), the new CARB limits for diesels will be 600 ppm, versus the more stringent 42 ppm for gas turbines.

The task of assessing the ship impact of a WIC retrofit has been superficially examined with respect to water needs, which appear manageable. It is expected that a typical speed profile for a DDG-Class ship traversing the 100-mile coastal zone will operate about 70% of the time at 20 knots (cruise), 20% of the time at about 12 knots and 10% of the time at 5 knots. The total time will be under 5.92 hrs and the total fuel consumption will be 26.4 long tons (lt). The ships service generator is assumed to operate at 2500 kW with overall fuel consumption of 4.5 lt, or a total of 30.8 lt. Water requirements for the WIC system will approximate the fuel requirements at 31 lt. Slower speed profiles will require less fuel, and therefore, less water.

A typical DDG is outfitted with two 12000-gal/day distillation plants. Each can produce 45 lt/day of water containing less than 1 ppm of total dissolved solids. Although General Electric has specified 0.1 ppm of total dissolved solids for continuous STIG engine operation (many thousands of hours per year), the total salt accumulation per gas turbine unit would be under 0.035 lbm during the few hours of traverse. Since salt is normally ingested via the input air and fuel streams, the LM2500 is washed down after 24 hrs of operation during regular service (this corresponds to washing down a unit every six days). Since a DDG will pass through a coastal zone once every six to twelve weeks, there will be about twelve additional washdowns per year.

Since the water purity level required for WIC-equipped diesel engines, are less exacting than the water purity level of gas turbines, potable water may be employed. Nevertheless, the diesel plants for seafaring ships will tap into the distilled water system in the same manner as proposed (vide infra) for the gas turbines. It is expected that prot-bound boats will utilize a separate water storage tank, equal in capacity to that of the fuel tank, replenished along with fuel, from at-dock, potable-water resources.

The water storage capabilities of a DDG are 60 lt in four tanks. The anticipated operational procedure would dedicate the water of two of the four distilled water tanks (about 30 lt) for water injection of two LM2500 units (only two units are required to maintain cruise speed) during the time of traverse of the coastal zone.

Engineering aspects of the fuel-injection system, the water system, the water feed manifold, monitoring systems for the NO_x, WIC system control, and shipboard testing need to be rigorously evaluated through analysis and operational investigation. Indeed, the aforementioned naval, at-sea, operating scenario for the reduction of NO_x has not been confirmed, either in simulation or test. The credibility of the water-injected combustor system, within the Navy community, as a viable alternative for acceptable NO_x reduction in the emissions of Navy gas turbines may be achieved only through a realistic shipboard evaluation.

7. Project Description:

The water-injected combustor approach to NO_x reduction in gas turbines will be evaluated in a shipboard configuration aboard a designated Navy destroyer or frigate on a routine mission.

The WIC-modified LM2500 (the 501K is not included in this project) gas turbine plant, and its components, the water-injected combustor, distillation plant, potable water storage tanks, an electronic feed control system, NO_x-monitoring equipment, and the impact of the WIC system on the ambient ship systems will be closely examined. The emission of NO_x from the gas turbine will be measured before entry into the coastal zone to establish a baseline reference condition. Measurements of the NO_x emissions will be automated to obtain a continuous record of emissions performance, which may ultimately be demanded by CARB. Real speed profiles will replicate the most likely naval experience.

The existing LM2500 combustors require orderly investigation of system hardware choices, system specification, and some fabrication of new components. Water feed will enter through the secondary row of fuel nozzles. Mixing and homogenization of water and fuel will be effected in a "tee" connection to the fuel manifold, which is adequate according to the manufacturer's (General Electric) experience.

Modification of water, and fuel feed pumps, and the electronic feed-control system (contractor supplied) will ensure conformity with the constraints of the gas turbine container and the ambient ship environment.

Modification of shipboard diesel engines for water injection will be explored at land-based facilities, in conjunction with contractors, who have already faced the problems of fuel-injector erosion and corrosion. The method of mixing the fuel will be investigated to avoid the unpredictable effects of slug flow, flame quenching, with consequent "missing" of cylinders, and loss of power. Fuel-water emulsion may be essential for predictable performance. methods of facilitating the emulsification process with detergents must be examined. The corrosive effects of detergents on the structural metals must be closely observed. Testing of diesel fuel injector configurations will take place largely in shoreside facilities pending successful resolution of fuel injector studies and tests.

Distilled water from the distillation plant will be manifolded to the potable water tanks with new valve controls dedicated to priority delivery of the distillate to new water-feed pumps during passage through the coastal zone. However, tests of the WIC system will be undertaken during regular cruise conditions with the permission of NAVSURFLANT and the ship commander.

Following each traverse of the coastal zone (and any other test), a washdown, examination, and a close analysis of the combustor for corrosion damage will occur. Corrosion could develop in the combustors of gas turbines, should the combustor be exposed to continuous, long-time, high levels of sodium exceeding 0.3 ppm of water, reduce the life of the engine, and invalidate the manufacturer's guarantees. Corrosion could limit the efficiency of fuel injectors in diesel engines with similar negative effects on guaranties.

The ship impact and influence factor of each element of the WIC system will be measured, in order to permit design of a fix should any problems arise.

The project will provide data on the performance of the WIC system with respect to reduction of emissions and efficiency during anticipated realistic operations. It will provide assessment of the corrosion resistance of the gas turbine exposed to marginally critical salt levels, and estimates of overall life cycle costs of the water-injected gas turbine, and estimates of the corrosion damage from water-fuel mixtures in the fuel injectors of diesels. The alternative NO_x-reduction methods will be assessed, because the scrubbing approach to diesel emissions will be proceeding simultaneously. The delivered products will include a credible statement of WIC characteristics, and a relative cost assessment of the alternative NO_x reduction systems. Based upon these experimental test data, and the relative cost estimates, a set of management recommendations will be offered to the Navy.

This project is in support of the Compliance Pillar in the Tri-Service Environmental R&D Strategic Plan.

8. Expected Payoff:

This project provides the Navy with a less risky, competitive, alternative retrofit of existing engines complying with EPA and CARB-mandated operational limits on the emission of NO_x from ship gas turbine power plants during traverse of the coastal zone. It will deliver data on the operational characteristics and relative merits of the water-injected combustor system for gas turbines, and fuel-plus-water injectors for diesels, providing reasonable bases for critical decisions necessary for complying with the CARB mandates.

9. Milestones:

0.	Initiate Program	09/94
1.	Develop Joint Navy-Contractor Strategy	10/94
2.	Commit the Navy to a Test Ship and Test Engine	10/94
3.	Identify Long Lead-Time Components and Systems	12/94
4.	Design Test Components and Test Monitoring Systems	03/95
5.	Modify Diesel Engine Fuel-Injectors	03/95
6.	Complete component Procurement Process	07/95
7.	Assemble Land-Based Systems (Turbine & Diesel)	09/96
8.	Test the Land-Based Systems	03/96
9.	Management Review and Go/No-Go Decision	05/96
10.	Modify the Test Ship Turbines for Water Injection	07/96
11.	Start Shipboard Tests	10/96
12.	Complete Shipboard Tests	01/97
13.	Report, Assessment and Management Review	04/97

10. Transition Plan:

Discussions with Contractor (General Electric Co., Allison Gas Turbine Co. and Detroit Diesel Co.) principals have been underway to determine whether the milestone schedule is not too compact. There is a verbal agreement over the participation of the Contractor and the forms of cooperation needed to facilitate the project.

The project will ultimately go forward to retrofit-system specification and fleet procurement of retrofit hardware for the water-injected gas turbines, and to recommendation of diesel modifications and a set of system layouts for Navy harbor craft.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	Total
SERDP	750	1200	850	500	3300
EPA	250	250	50	50	600
DON	0	0	150	250	400
Total	1000	1450	1050	800	4300

12. Performers:

Participants in the study include CDNSWC, U.S. EPA, MEERL, MD-4, the Norfolk Naval Shipyard, and contractors. Program management, development facilities, land-based LM2500 and 501K test engines, a Navy diesel test engine, distilled water system components, and NO_x-monitoring systems will be supplied by the CDNSWC. Water feed manifold(s), manifold interconnections, and the electronic water and fuel control system will be provided by the Contractor(s). Installation of shipboard gas turbine manifolds, and water manifolds will be performed by the Norfolk Naval Shipyard. NAVSURFLANT will designate a test ship for evaluation.

13. Principal Investigators:

Dr. Herman B. Urbach
Naval Surface Warfare Center
Carderock Division
Annapolis Detachment, Code 82T
3A Leggett Circle
Annapolis, MD 21402-5067
TEL: (410) 267-2864
FAX: (410) 267-3553

Mr. John H. Wasser
U.S. EPA
AEERL, MD-65
Research Triangle Park, NC 27711
TEL: (919) 541-2476

14. Keywords:

Gas turbine, Diesels, NO_x emissions, Water injection

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Lead-Based Paint Hazard Mitigation

3. **Agency:** U.S. Army Corps of Engineers

4. **Laboratory:** Construction Engineering Research Laboratories (USACERL)

5. **Proposal ID:** #521

6. **Problem Statement:**

The DoD wide lead-based paint (LBP) hazard mitigation cost has been estimated to be more than $1 billion over the next 10 years. The increased cost for LBP abatement is due to the additional requirements for containment of dust/waste, environmental monitoring, worker protection, and record keeping. Human exposure to lead is associated with adverse health effects, including permanent damage to the central nervous system. About 75% of all homes constructed in the United States before 1980 have some LBP. While many sources of lead exposure exist, lead from lead-based paint is the most significant source of exposure at DoD installations. Although lead is no longer used in house paints and the application of lead primers on steel structures is declining, old paints with hazardous levels of lead remain on many surfaces today. Traditional methods of paint removal, such as abrasive blasting, or chemical stripping, can be used to remove LBP. However, the costs of containment, worker protection, and waste disposal make many of these traditional methods cost prohibitive where the paint contains lead. The overall goal of this project is to develop improved methods for LBP hazard mitigation to reduce costs and enable compliance. The majority of the work in this proposal falls under Applied Research/Technology Demonstration/Technology Transfer (6.2/6.3).

This is an enhancement of a funded SERDP FY93 project titled "Glassy Materials Modeling for Hazardous Waste Immobilization".

7. **Project Description:**

This SERDP project is in support of Tri-Service Environmental Quality Strategic Plan (Green Book) Requirement Thrust 2.L.5a: Satisfy RCRA (Treatment/disposal of Operations Waste). Furthermore, this work addresses Army-wide Prioritized Requirement Statements, Compliance 2.3.k Lead-Based Paint Testing/Disposal, Compliance 2.5.a Lead-Based Paint Removal, Compliance 2.6.a Find Abrasive Substitutes for Removing Paint; and Pollution Prevention 3.2.c. Cost Effective Lead-Based Paint Abatement.

This is an integrated multi-disciplinary, multi-agency project. The technical objectives of this project are (a) to develop novel vitrification technology for lead-based paint removal that can be used effectively for immobilization of heavy metal hazardous waste (b) to evaluate the use of new abrasive sponge blasting media for lead-based paint removal (c) to develop a robotic system for removal of lead-based paint and (d) to develop and demonstrate an integrated "Lead Hazard Mitigation and Management System (LMS)". Objective (a) will minimize the amount of hazardous waste produced during LBP removal. Objectives (b) and (c) focus on improving worker and public safety. Finally, objective (d) will assist installations in developing the most

cost effective LBP hazard mitigation strategy. The technical approach for this project will be phased to include the following:

a. Glassy Materials Modeling for Hazardous Waste Immobilization.

Heavy metal hazardous waste residues have been effectively vitrified in situ in the matrix of glassy materials. The actual mechanisms by which these materials are immobilized have not yet been determined. Laboratory experiments have determined that bonds within the glass network break, providing bonding sites within this network for the heavy metal cations. Similarly, the cations may become part of the lattice structure by randomly occupying interstitial and/or defect sites. The Resource Conservation and Recovery Act (RCRA) mandated Land Ban requires that hazardous waste be treated to below the characteristic level prior to disposal. The long term durability of the vitrified and stabilized wasteforms needs to be evaluated so that the leaching behavior of materials under actual field conditions can be modeled and predicted.

The technical approach will involve the preparation of vitrified materials containing heavy metal hazardous waste and determining through characterization techniques such as X-ray diffraction (XRD), X-ray Spectrometry (XRS), Scanning Electron Microscope (SEM), how the hazardous waste is incorporated within the glass structure and immobilized. The mechanisms of the vitrification and ion leaching processes will be modeled to optimize hazardous waste immobilization. The tetrahedral structure, bond angles, and ionic field strengths of the glass forming and glass modifying oxides will be investigated. One application process, is to thermally spray a molten glass compound directly onto a lead containing substrate. This has shown the potential to effectively contain the hazardous waste residues. The mechanism by which heavy metals become immobilized will be investigated. Existing and recently developed laboratory tests will be used to predict the long term durability of the vitrified wasteform.

A paper titled "Vitrification of Lead Contained in Lead Based Organic Coatings Using Thermal Spray Technology" was presented at the ASTM sponsored Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Waste, held in Williamsburg, VA, 1 November 1993. A patent application titled "Removal of Lead Based Coatings by Vitrification Using Thermal Spray" has been filed.

b. Sponge Blasting.

USACERL is evaluating emerging technologies for the removal of lead-based paint from DoD buildings and structures. The technologies being evaluated include cryogenic blasting, laser paint removal, chemical stabilizers, alternate chemical strippers, and confined hydraulic blasting. The sponge media blasting technique appears to be particularly promising for LBP removal from surfaces of buildings. Soft (sponge) media abrasive products have been developed to address issues of worker and public safety, hazardous waste minimization, and pollution prevention. The sponge media consists of a matrix of water-based urethane foam within which the abrasive particles are dispersed. The media can be wet with water or chemical solutions to increase productivity. The aggressiveness of the sponge media can be tailored for the specific application by changing the characteristics of the abrasive particles inside the urethane foam. For the field demonstration of emerging LBP technologies, sites will be selected from typical building surfaces. Pre-abatement testing of the structures will be done to characterize the painted surface, including paint thickness, type, and uniformity. Post-abatement tests will be done to determine how efficiently the paint removal is performed from the viewpoint of completeness of the lead

removal. Hazardous wastes will be carefully contained, collected, tested, and disposed. Cost data will be recorded for all work phases and the performance envelope will be validated.

c. Robotic Paint Removal System.

USACERL is developing an automated platform which will use plastic media blasting for removal of lead-based paint from interior of buildings. Another automated technology being developed is a portable thermal spray system which could be used for vitrification. Robotics technology is particularly well suited for simple, repetitive tasks such as paint removal. Additionally, a complete collection of blast wastes and dust is possible with a simple recovery apparatus. These systems will be integrated with sensors. A practical robotic paint removal system will be assembled, resulting in a low cost, environmentally safe LBP removal. The mobile robotic platform will be equipped with necessary sensors, controllers, blasting nozzle, abrasive media feeder and a vacuum waste collector to complete a functional robotic system. The robotic paint removal system will be evaluated using the sponge media and more traditional abrasives such as coal slag and steel shot. After laboratory evaluation, the robotic paint removal system will be field tested at DoD installations to establish the technical validity and cost-effectiveness.

d. Lead Hazard Mitigation Management System (LMS).

A Lead Hazard Mitigation Management System (LMS) will be developed to assist engineers in developing the best LBP abatement strategy for their specific installation. The system will provide assistance with (1) installation-wide prioritization of abatement projects, and (2) selection of the best abatement method for a given situation. User inputs to LMS will include (1) a structure inventory which catalogs background information such as substrate type, building use, and age, and (2) field test information such as identification of potential lead-based paint hazards, lead testing results, and coating condition index. LMS will utilize the user-provided data in conjunction with knowledge bases containing information on regulations, abatement technologies, risk assessment, waste management, and cost to generate the best abatement strategy. LMS will be highly interactive and will allow the user to "test" various alternatives. The knowledge base will be able to be updated as new hazard assessment and abatement technologies emerge or as regulations change. LMS will also assist in providing information to occupants and workers to reduce the panic that is often associated with LBP abatement projects. The technical approach will include development of the inventory and field test databases to include all information that is required for decision making; development of the knowledge bases; development of methodologies and decision trees for prioritization and alternative selection; development of occupant & worker support packages; LMS software development; demonstration of LMS at a DoD installation; and publication and documentation of results.

Key technology barriers which need to be overcome are: prediction of the long term durability of the vitrified glass, mechanisms of leaching of stabilized wasteform, urethane foam abrasives, and robotics and sensor systems integration. The proposed research has many innovative and novel aspects and therefore, the probability of overcoming these barriers is high. This project has a low risk and high payoff.

8. Expected Payoff:

The urgency of the lead-based paint problem has increased due to the Base Realignment and Closure Act, where the installations are required to abate their residential buildings of lead-based

paint. The DoD wide cost of lead-based paint hazard mitigation is estimated to be more than $1 billion, therefore it is imperative that effective decision making tools be utilized to ensure that the most cost effective, environmentally safe project plans are developed using emerging technologies. The proposed lead paint removal technologies combine the advantages of robotics with sponge media blasting and with in situ vitrification. If we assume 10% reduction in this cost then the return on investment is approximately 25:1.

Use of the LMS integrated hazard abatement strategy will allow full consideration of appropriate abatement technologies, installation budget, scheduling constraints, occupant management, and master maintenance plan. The ultimate payoff is that this project would provide valuable assistance to insure that a DoD installation is not in violation of regulatory requirements for lead-based paint hazard mitigation, as well provide healthier homes to military service members and their families.

9. Milestones:

1.	Prepare vitrified materials	06/94
2.	Lab Study of Varied Processing Parameters	09/94
3.	Investigate Microstructure through Characterization	09/95
4.	Complete evaluation of Sponge Media	06/96
5.	Complete Glassy Materials	07/96
6.	Develop the alpha version of LMS	09/96
7.	Complete Robotics system prototype tests	03/97
8.	Complete Field Tests and Demonstrations	06/97
9.	Complete Reports and Technology Transfer Documents	09/98

10. Transition Plan:

Demonstrations of vitrification and sponge blasting in conjunction with robotics will be conducted at DoD installations. LMS will be implemented, from assessment to the production of the hazard mitigation strategy, at a DoD installation. In order to transfer the methods and technologies developed in this program an intense documentation effort will be required and full coordination will be achieved through the "DoD Interagency Lead-Based Paint Task Force". Tri-service guidance documents including Engineering Technical Letters, Guide Specifications, User Guides, and Technical Manuals will be prepared for the use of DoD installations.

The technologies developed and demonstrated under this SERDP project have dual use application in the Department of Housing and Urban Development (HUD).

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	700	650	700	600	500	3300
DA	310	0	0	0	0	740
TOTAL	1010	650	700	600	500	4040

12. Performers:

U.S. Army Construction Engineering Research Laboratories, Champaign, Illinois, will be the lead laboratory. Other performers in this project are the U.S. Environmental Protection Agency, Risk Reduction Research Laboratory (POC: Ms. Diana Kirk); and DOE Lawrence Livermore National Laboratory (POC: Mr. Tehmau Kan). Academic involvement includes but is not limited to University of Illinois. Industry involvement includes but is not limited to TDJ Group, Strip It, and APS Materials. The work in this project has a high potential for a CRADA with the industry.

13. Principal Investigator:

Dr. Ashok Kumar
U.S. Army CERL
P.O. BOX 9005
Champaign, IL 61826-9005
Phone: (217) 373-7235
FAX: (217) 373-7222

14. Keywords:

Vitrification, Leaching, Modeling, Hazardous, Robotics, Lead Abatement

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Emission Reduction Planning Model

3. **Agency:** Air Force

4. **Laboratory:** Armstrong

5. **Proposal ID:** #175

6. **Problem Statement:**

The 1990 Clean Air Act Amendments (CAAA-90), the first major revisions to federal air legislation since 1977, mandate a substantially more complex air pollution compliance program. Title III (Air Toxics Provisions) and Title V (Permit Provisions) of the CAAA-90 present especially difficult, long-term compliance challenges for Department of Defense (DoD) installations. Although air pollution programs at DoD facilities are similar in that they consider similar sources, the program at any site must consider specific local conditions. These conditions include the number and type of air pollution sources, operation and maintenance activities, the facility's mission, and the regulatory environment to include both regional and local concerns. Prevention, minimization, and control of pollution, as well as administrative management, are all components of an optimal, cost-effective compliance strategy. Development of a compliance strategy can become overwhelming for DoD environmental personnel at the base level due to the complexity of the problem and possible solution approaches. Poorly planned compliance strategies can lead to (i) non-compliance with air pollution regulations, (ii) mission impairment from regulatory action (notice of violation, fine, activity limitation, shutdown), or (iii) excessively expensive or inappropriate solutions. Conversely, well-planned, cost-effective compliance strategies will avoid compliance problems, leading to enhanced relationships with regulatory agencies and surrounding communities, as well as reducing air pollution.

Previous funding for the Emission Reduction Planning Model (ERPM) has led to the development of a prototype decision support system. A full-scale decision support system for establishing and maintaining optimal, cost-effective compliance strategies would greatly aid environmental personnel in developing appropriate compliance strategies. Funds are requested to expand an existing joint Air Force/Army/EPA applied research initiative and to support the demonstration of the ERPM at several federal facilities.

7. **Project Description:**

a. Technical Objective: The objective of this project is to develop a state-of-the-art decision support system to aid environmental personnel in reducing air pollution compliance problems. The availability of such a system will allow for consistent, optimal, and cost-effective application of control technologies, prevention measures, and mitigation techniques. The proposed decision support system is intended to support, not replace, experienced environmental personnel.

b. Technical Approach: To date, the ERPM research program has resulted in the development of a prototype decision support system. The prototype system tested assumptions on how to encode facts, relationships, and inference methods required to develop air pollution compliance

strategies. The prototype system, while small in scale, has demonstrated that a decision support system of this type is feasible and potentially very useful for developing compliance strategies.

The full-scale decision support system will follow design and function of the prototype system. Algorithms based upon EPA, DOE, and DoD expertise will be constructed to assess current base emissions, applicable regulations, available control devices, and compliance alternatives (i.e., pollution prevention, pollution minimization, and administrative techniques) in order to recommend prioritized actions that optimize regulatory, economic, and environmental benefits. Draft software packages will be user tested at selected Air Force and Army installations to gain insight for improving system utility and ease of operation.

c. Technical Challenges: The primary technical challenge will be integrating expert system algorithms with external databases and pre-existing models. Secondary challenges include obtaining acceptable execution times on a user-friendly software platform.

d. Tasks: Phase I of the project will include the incorporation of control technologies and federal regulations into the decision support system as well as the development of an interface with existing emission inventory databases and dispersion screening models. Phase I will be completed with an in-house review of work to that point and a field demonstration of the phase I decision support system.

Incorporating control technologies into the decision support system involves a survey of the state-of-the-art control devices. Both criteria pollutants and air toxics will be considered for each source category as control devices often affect more than one pollutant. A broad spectrum of alternatives will be considered so that the most cost-effective and environmentally acceptable approaches are identified. As each of the various control devices for each source category are specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Incorporating applicable federal regulations into the decision support system involves a survey of the regulations that apply to various sources present at federal facilities. As regulations are identified, the expert-system rules associated with these regulations will be developed and implemented into the decision support system.

Development of an interface with existing emission inventory database systems (e.g., AQUIS, APES, etc.) will allow the decision support system to take advantage of the vast number of source and emissions data that are available in emission inventory databases. The interfaces will prevent the duplication of functions already performed by emission inventory database systems such as estimating emissions.

Developing an interface with dispersion screening models will provide a link between source emissions and regulations based on ambient air quality standards. The screening technique will provide a conservative estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed control technology's efficiency will be sufficient to meet an applicable ambient standard.

Phase II of the project will include the incorporation of compliance strategies beyond control technologies into the decision support system, and the development of an interface with advanced EPA-approved dispersion models.

Phase II will be completed with a field demonstration of the entire decision support system. Once the phase II field demonstration is complete, modifications to the decision support system will be affected and the final software package, documentation and report will be prepared.

Incorporating compliance strategies beyond control technologies involves a survey of pollution prevention, pollution minimization, and administrative management techniques that are applicable to DoD facilities. Optimal, cost-effective and environmentally acceptable compliance strategies can only be developed when considering this complete range of compliance methods. As each of the various compliance strategies for each source category is specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Developing an interface with advanced EPA-approved dispersion models will provide a link between source emissions and regulations based on ambient air quality standards. The incorporation of dispersion modeling capability will provide a more accurate estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed compliance strategy will be sufficient to meet an applicable ambient standard.

e. Relationship to DoD Environmental Objectives: This project directly supports Tri-Service Environmental Quality Strategic Plan requirements 2.I.2.e, DoD-Wide Emission Management System and Database, and 2.I.2.k, Assess Atmospheric Impact of Air Base and Aircraft Operations for Compliance with CAA and for EIAP.

8. Expected Payoff:

This project will ultimately provide a state-of-the-art decision support system to aid environmental personnel in determining areas of potential violations and compliance options, thus leading to installation-specific, cost-effective air pollution compliance strategies. Moreover, DoD-wide use of the decision support system will provide consistency in the treatment of air pollution problems. The decision support system will be designed to easily adapt to other industries as well as to the needs of local, state, and federal regulatory agencies. Further, incorporating EPA-approved methodologies in the decision support system will help to expedite the regulatory acceptance of a facility's compliance strategy. Finally, the design of the decision support system allows for its application many years into the future, and easy integration of new compliance strategies and regulations.

9. Milestones:

1.	Incorporate Control Technologies/Federal Regulations	09/94
2.	Interface with Emission inventory databases/dispersion screening model	12/94
3.	Complete Phase I internal review	03/95
4.	Complete Phase I field demonstration	09/95
5.	Modify per Phase I feedback	12/95
6.	Incorporate Alternative Compliance Strategies	02/96
7.	Complete Advanced Dispersion Model Interface	03/96
8.	Complete Phase II field demonstration	06/96
9.	Modify per Phase II feedback	09/96
10.	Completed Software/Documentation/Final Report	09/96

10. Transition Plan:

The resultant decision support system will be implemented at Air Force and Army installations throughout the United States via the Air Force Center for Environmental Excellence (AFCEE) and Army Environmental Center (AEC), respectively, as well as potential application by DOE and other federal agencies. Further, there exists significant potential for EPA adoption as an accepted and encouraged means of compliance evaluation and planning.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	200	300	400	900
Air Force S&T	201	0	0	373
Army S&T	190	205	0	470
EPA	0	0	0	15
Total Project	591	505	400	1758

12. Performers:

The Environics Directorate of Armstrong Laboratory (AL/EQ)will coordinate this development effort with the Army's Construction Engineering Research Laboratories, Department of Energy's Argonne National Laboratory, and the Environmental Protection Agency's Air and Energy Engineering Research Laboratory.

13. Principal Investigators:

Capt Mike Jones
AL/EQS
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
TEL: (904) 283-6249
FAX: (904) 283-6286

Secondary POC:
Mr. Mike Kemme
USACERL
TEL: (217) 373-3485

14. Keywords:

Air Pollution, Compliance, Planning, Emissions, Controls, Model.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Laser Ablation/Ionization Characterization of Solids

3. **Agency:** Department of Energy

4. **Laboratory:** Pacific Northwest Laboratory

5. **Agency Proposal ID:** #362

6. **Problem Statement:**

The Department of Energy is currently undertaking the enormous task of remediating defense wastes and environmental insults which have occurred over 50 years of weapons production. It is abundantly clear that significant technology advances are needed to characterize, process, and store highly radioactive waste and to remediate contaminated zones. Aside from the processing and waste form issues, analytical technologies needed for the characterization of solids, and for monitoring storage tanks and contaminated sites do not exist or are currently labor-intensive tasks. The purpose of this research is to develop widely applicable mass spectrometry techniques for analysis of mixed chemical wastes. The sensitive and rapid analysis of organics, inorganics, and TRU's in contaminated soils, groundwater, and in tank wastes is a key Hanford-site need. The urgent need for this work has been highlighted by recent findings of the DNFSB, and by the agreement between the DOE, EPA, and Washington State.

The remediation of Hanford-site defense waste and long-term disposal of high-level mixed wastes requires chemical analysis of the waste streams. The projected costs of these tasks, with current methods, is in excess of $500M. Analysis of mixed waste is needed to characterize the chemical classes and concentrations of a wide variety of waste materials. Tank and crib waste sites contain broad distributions of both organic compounds; aromatics, nitrates, chelating agents, and halogenated hydrocarbons, and inorganic compounds; chromates, ferrocyanides, metals, and TRU;s. The chemical speciation and concentration of these materials must be determined in order to design effective clean-up strategies. Additionally, the high concentrations of radioactive waste materials, in tanks and cribs, provide an energetic driving force that continuously transforms mixed waste in complex kinetic pathways. Hence, analyses need to be made in a timely fashion. Current methods require as much as six months for a single waste tank core sample analysis and report. Initial research will develop rapid laser-based analysis techniques, the principles of which may be extended to on-line field measurements.

This research impacts needs in both basic and applied research categories and will help determine the design parameters and evolution of field analytical platforms. The hot cell and field instruments being developed under the DOE/Hanford Mobile Analytical Reconnaissance System (AMRS) program constitutes a major effort in meeting Hanford-site remote analytical and characterization needs. The proposed research is part of an existing SERDP program designed to conduct fundamental studies in support of the MARS program. It is currently operating under SERDP FY93 funds. Significant progress has occurred in the previous FY. This includes the assembly and testing of the ultra-high-vacuum laser ablation chamber, the design and construction of the time-of-flight mass spectrometer, and initial experiments on laser ablation of simulated tank waste forms.

For certain critical trace elements, it will also be important to focus on the method of ionization of the ablated material. Technetium-99 has been identified as a significant ground water contaminant at a number of locations on the Hanford Site. Because of its long half-life (214,000 years), high fission yield, and high rate of mobility in the subsurface, Technetium-99 is considered a hazardous radioisotope waste. Furthermore, Technetium-99 can be used as a critical path isotope for performance assessment of nuclear waste isolation barriers. Because Tc-99 is a long-lived pure beta-emitter, routinely available radiochemical counting methods do not provide adequate sensitivity for use of Tc-99 as a performance assessment tool. However, the long half-life of Tc-99 does make it an ideal case for high-sensitivity detection by laser resonance ionization methods, which are responsive to the quantity of atoms present rather than the radioactive decay rate. Pioneering work conducted at Johannes Gutenberg Universitat Mainz in Germany has demonstrated that multiple-resonance laser induced ionization techniques can be successfully applied to the measurement of Tc-99 in environmental samples. In the previous fiscal year, our capabilities for detection of technetium have advanced in that a large number of possible excitation schemes have been investigated to optimize the overall efficiency and to suppress unwanted non-resonant ionization of other species. To date, the best excitation scheme involves a three step (3 laser) excitation into an autoionizing state using wavelengths of 313.2, 821.1, and 670.7 nm. Current investigations are designed to determine optimal excitation schemes, using resonances that overlap the emission wavelengths of reliable diode and titanium-sapphire laser sources. Improvements on this methodology, are expected to ultimately result in a field-portable, routine analytical technology capable of rapid, accurate and sensitive measurements.

The major objectives of this research are:

1) To develop general and sensitive techniques for determining the molecular speciation of organics and inorganics in tank wastes and those chemisorbed on mineral soil substrates. these methods must be sensitive to a broad spectrum of compounds to detect the many species present in mixed waste environments.
2) To develop new methods for the detection of technetium. Development of multiphoton-ionization techniques is required to satisfy the critical need for sensitive and rapid detection of Tc-99. Current methods require weeks, laser analysis can be completed in hours.
3) to transfer this new knowledge to other applied DOE analytical programs such as MARS.

7. Project Description:

Laser-based analysis techniques are proposed to achieve these goals, primarily laser ablation mass spectroscopy (LAMS) and resonance enhanced multiple photon ionization (REMPI). Laser ablation can vaporize nearly any solid material in pulsed plumes of sufficient concentration for detailed analysis by mass spectrometry, laser-induced fluorescence, and other techniques. The LAMS approach couples laser vaporization with ultrasensitive mass spectrometry. Analysis of even complex, multicomponent mixtures can be performed rapidly and requires very little sample. This is highly desirable for the analysis of many environmental samples and hazardous wastes. When the concentrated laser ablation pulses are combined with multiphoton ionization time-of-flight mass spectroscopy, the result is a versatile and sensitive analysis techniques of very high mass resolution. The excellent mass resolution provides superb differentiation between compounds of similar masses and between isotopes. In addition, the resonant ionization process can provide excellent spectral resolution which extends and compliments the mass resolution. These features are crucial for the successful chemical speciation of complex waste samples.

The advantages of the LAMS approach include: Small sample requirements, minimum sample preprocessing, minimum waste generation, and reliable technology. However, several uncertainties are introduced by the ablation process. For instance, it is to clear how well the composition of the ablated (gaseous) products reflects the sample composition; some sample components can be preferentially ablated. Changes in the chemical state (e.g., changes in the oxidation state of metals) in the solid and gas phase are also potential problems. We propose to use several concurrent approaches to determine in more detail the mechanisms and consequences of laser ablation on model samples of simulated waste, and on relevant wide band gap inorganic materials, with and without chemisorbed species. Of particular importance are the effects of the ablation process, the defect-mediated coupling of light into the solid, the mechanism of particle emission, and particle interactions after emission but prior to the actual analysis.

The analysis of organic species chemisorbed on mineral substrates is an extremely import application of laser analysis techniques due to the need to detect toxic wastes contained in soils for waste characterization and environmental compliance. Many organic waste compounds absorb strongly in the UV (e.g., trimethylamine, benzene, naphthalene, toluene, phenol, and chlorinated aromatics) and may prove especially amenable to laser techniques. The mechanisms of desorption and ionization of such molecules on macroscopic single crystals of MgO, quartz, $NaNO_3$, and $CaCO_3$ would also aid analysis. Developing quantitative analytical methods requires the study of both neutral and ionic species desorbed from the surface, their kinetic energies, and possible electronic excitations (gas phase luminescence studies) as a function of laser fluence and wavelength.

Technetium-99 measurement systems to be addressed by this project will expand upon existing expertise and technology that has been developed at Pacific Northwest Laboratory (PNL). Resonance enhanced multiphoton ionization, coupled with mass spectrometry, has been shown to be an extremely sensitive and selective approach to the analysis of rare isotopes. This work at PNL has emphasized the use of high-resolution continuous-wave lasers to simultaneously maximize isotopic selectivity and absolute sensitivity, and has demonstrated detection limits in the attogram (10^{-18}g) range and the ability to detect a target isotope in the presence of a 10^{10} or greater excess of other isotopes of the same element. Applying these methods to the measurement of Tc-99 will initially involve offsite assignment of B.A. Bushaw at Universitat-Mainz to understand the spectroscopy, thermal atomization dynamics, and handling and preparation of environmental technetium samples. Working in collaboration with the researchers at mainz (and taking advantage of their existing experience) will facilitate the rapid development of specific excitation schemes and measurement procedures that can be addressed with compact solid state laser systems. Solid state laser technology has the advantage that it is reliable and easily incorporated into field analytical instrumentation.

8. Expected Payoff:

These programs will increase our capabilities to analyze mixed waste and detect Technetium. The results will be useful in performing the analysis of tank and crib wastes and contaminated soils and groundwater. The near real-time analysis capabilities of these methods will also be important for monitoring waste retrieval, facilities decontamination, and other site restoration actions. It will contribute to the success of the MARS program which is predicted to result in a savings of $30-75M during the first three years following its implementation. Similar percentage savings can be expected at other DoD and DOE sites.

9. Milestones:

1.	Implement and characterize time-of-flight detection of model waste simulant materials	12/94
2.	Determine optimal laser-ionization frequency and pulse duration	2/95
3.	Develop a cw diode laser scheme for excitation of Technetium	2/95
4.	Calibrate individual waste compounds	3/95
5.	Evaluate application to complex waste simulant	9/95
6.	Report interim results to MARS Program	10/95

10. Transition Plan:

Key to the impact of this project is the teaming of the end user (WHC and PNL staff from the AMRS and related programs), and the SERDP scientific staff. The MARS team provides the engineering staff who have extensive experience in the development and delivery of highly technical, on-line, field and mobile instrumentation for the DOE and DoD. They are also in direct contact with potential industrial partners for the eventual production of instrumentation at Hanford and other federal facilities. Through this approach the findings of the SERDP program will be readily available to the end users.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	380	410	340	0	1347
DOE*	425	425	425	0	1700
TOTAL	825	835	765	0	3047

*MARS related technology development program.

12. Performers:

The organizations performing the work are: The Department of Energy, Division of Basic Energy Research, and Pacific Northwest Laboratory operated by Battelle Memorial Institute. A major beneficiary is the DOE MARS Program managed by PNL for the DOE.

13. Principal Investigator:

Dr. Steven D. Colson
Pacific Northwest Laboratory, Molecular Science Research Center
PO Box 999, MS K2-14
Richland, WA 99352
Telephone: (509) 375-6882 Facsimile: (509) 375-6916

14. Keywords:

Mixed-waste, Analysis, Laser-ablation, Ionization, Characterization, Technetium.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Vapor Permeation VOC Recovery from Refueling and Storage (VOC Control Fueling/Fuel Storage Operations)

3. **Agency:** USEPA

4. **Laboratory:** Risk Reduction Engineering Laboratory

5. **Proposal ID:** #252

6. **Problem Statement:**

Ocean tankers and storage tanks for petroleum products such as gasoline, diesel fuel, or aviation fuel, emit a large amount of the lighter fraction of the fuel through evaporation during filling and storage process. While the evaporative losses can be a health-hazard to workers and the neighborhood, the economic loss is large and unnecessary. Thin-film non-porous membranes specially made of a hydrophobic resin are capable of recovering the volatile organic compounds (VOCs) from petroleum for direct recycle/reuse. In the vapor permeation process, the VOCs are removed from the VOC-air mixture and condensed back to a liquid phase with very high selectivity.

This is an applied research [i.e., 6.2] project. It is an effort recommended for inclusion in the EQ Strat Plan by the Naval Civil Engineering laboratory (NCEL, now the NFESC). It addresses SERDP Thrust 2.D; Other Hazardous Wastes and supports the SERDP goal to develop affordable and effective control technology for priority pollutants emitted from operations and training activities. Because of its importance to the DoD, it is scheduled using the accelerated program description chart of the EQ Strat Plan (p.II.98).

7. **Project Description:**

VOCs from air can be recovered by simple condensation. When the VOC in the air is dilute, which would be the case when VOCs are lost to air during filling a tanker or a storage tank, direct condensation is not practical because of the large air volume involved. It would however be economical if the VOCs can be concentrated by a factor of 1000 or more before condensing. Such is the purpose of the use of vapor permeation membranes.

The process of vapor permeation is very similar to pervaporation, which is usually reserved for VOC-recovery from a liquid stream. In both processes, the membrane is hydrophobic and non-porous. The hydrophobic VOCs must first dissolve in the membrane itself. This phenomenon of absorption is characterized by Henry's Law, and a constant, Henry's Law constant, represents the efficiency of adsorption. The VOC then diffuses through the thickness of the membranes and finally desorbs at the permeating side of the membrane. A vacuum is usually applied and a condenser condenses the VOCs. An inert gas sweep can also be used to achieve similar, and in some cases, superior results. The energy for evaporation generally needs to be provided, although in the case of vapor permeation, the energy demand is much lower than pervaporation, since the VOCs are already in vapor phase.

Some amount of research has been done on the recovery of VOCs, chiefly chlorofluorcarbons (CFCs), from air by vapor permeation process. The present research involves:

1. Characterizing the chemical composition of VOC emissions from petroleum, and determining the kind of membranes needed to apply vapor permeation. The latter will involve screening adsorption studies (Henry's Law constants measurements);
2. Constructing a laboratory apparatus to conduct vapor permeation experiments on simulated VOC emissions, and modeling the permeation process for predicting performance of a scaled-up prototype;
3. Constructing membrane modules for the purpose;
4. Preparing an economic analysis to determine capital requirement and payback period; and
5. Demonstrating the technology with a prototype.

Part 1 of this research will be conducted in EPA-RREL. The expertise exists for conducting bench-scale research on vapor permeation (and pervaporation), and for casting specialty membranes. A bench-scale adsorption study will be done using a microbalance to measure minute mass differences of membrane fragments. The modeling that is involved is only an extension of work previously performed in the RREL on a pervaporation project in cooperation with the University of Cincinnati. Part 2 will also be done in-house in RREL. Part 3,4 and 5 will be contracted out. Research-based membrane companies, such as Membrane Technology and Research (MTR, Inc.), Palo Alto, CA, are particularly equipped to conduct these parts most efficiently and cost-effectively. MTR, Inc., for instance, is collaborating with Hoecht-Celanese for large-scale demonstration of pervaporation processes.

The technical risk of this proposed approach is low. The project addresses the Tri-service Environmental R&D Environmental Plan Requirement (2.I.1.o); Control Emissions from Energetics manufacturing and stationary sources.

8. Expected Payoff:

The VOC removal is needed to reduce the formation of photochemical smog and ozone non-abatement.

9. Milestones:

Year 1: Complete part 1., complete design and fabrication of apparatus, and complete the economic study extramurally.
Year 2: Complete bench-scale study, and complete design of prototype
Year 3: Complete field study.

10. Transition Plan:

Design data and results of demonstrations will be provide to DoD during the third year. The project will be coordinated with the NFESC for the development of User Data Packages and technology transfer needed to communicate the technology development results in a form that will enhance DoD-wide exploitation. Although newly formed,the NFESC has excellent capabilities to assist in the RD&E efforts and will become the primary technology transfer vehicle as the technology moves from the research through the field study phase.

11. Funding: ($K)

	FY94	FY95	FY96	Total
RREL-EPA	200	450	150	800
NFESC	50	50	50	150
Total	250	500	200	950

12. Performers:

Part 1 and 2 will be done in-house in RREL-EPA. Parts 3-5 will be contracted out for demonstrating the technology. NFESC will collaborate with RREL in parts 1 and 2, and will closely monitor the pilot and demonstration work that follows.

Ms. Jennie Koff, NFESC
Code ESC 421jk, 560 Center Drive
The Naval Facilities Engineering Service Center
Port Hueneme, CA 93043-4328
TEL: (805) 982-1674
FAX: (805) 982-1409

13. Principal Investigator:

Dr. Subhas K. Sikdar
USEPA; Office of Research and Development
Water and Hazardous Waste Treatment Research Division
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268
TEL: (513) 569-7528
FAX: (513) 569-7787

14. Keywords:

Pervaporation, vapor permeation, hydrophobic membrane, hydrocarbon recovery.

At the time of printing, a detailed project description had not been received for:

Solid Waste Encapsulation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Advanced Mass Spectrometry for Atmospheric Monitoring

3. **Agency:** US Air Force

4. **Laboratory:** Armstrong Laboratory, AL/XP

5. **Proposal ID:** #192

6. **Problem Statement:**

The need for accurate measurements of the identity, concentration, and spatial distribution of atmospheric pollutant species is fundamental to many areas of environmental research and development and crosses the boundaries of several of the SERDP pillars:

- Compliance with standards for emission of pollutants into the air from waste sites, rocket and jet engine operations, power plants, manufacturing and weapons destruction facilities, etc., can only be demonstrated by the use of reliable measurements of the emissions.

- Air pollution reduction efforts must be founded on accurate assessments of current emission levels and must be monitored for effectiveness.

- Cleanup of underground hazardous waste sites requires first that the sites be found and characterized. Detection of airborne emissions from such sites is an efficient and cost-effective alternative to traditional bore hole drilling methods.

The goal of the research proposed here is to develop and demonstrate technology to measure the concentrations of essentially all neutral species in the atmosphere at ground level, in the troposphere, and in the stratosphere. Traditional mass spectrometry for detection of major pollutant species such as CO_2 and NO_x will be combined in a single instrument with a novel chemical ionization technique for ultra-high sensitivity detection of trace neutrals. The technique is broadly applicable to the many requirements listed above, is adaptable to field measurements on the ground and on research aircraft, is low risk, and provides greater than 10^{12} dynamic range with part-per-trillion sensitivity.

7. **Project Description:**

Approach: In recent years the range of techniques available for analysis of natural and pollutant species in the troposphere and stratosphere has expanded. In particular, ion mass spectrometry techniques have become much more sensitive and, in combination with laboratory kinetics measurements, have led to the quantitative analysis of trace neutral species present in concentrations much too small for direct measurement by traditional mass spectrometry.

Chemical reactions between neutral pollutant gas molecules and the ions that are naturally present in the atmosphere frequently produce new ion species that are unique signatures of the original trace neutral. Detection of the product ion species unambiguously shows the presence

of the original neutral. The concentration of the neutral species can be calculated from the intensities of the reactant and product ions measured in the atmospheric environment of interest and from measurements of the rate coefficients of the relevant ion-molecule reactions. This technique has been used to determine the concentrations of such species as sulfuric acid, nitric acid, pyridine, and picoline in the unperturbed atmosphere and to measure the concentration of the important hydroxyl radical (OH), which cannot be detected easily by other methods. Because of the very small background signal level for ions, the technique routinely gives sensitivities in the part-per-trillion range and can sometimes be optimized to detect neutrals in parts-per-quadrillion.

Several novel techniques for making very high sensitivity measurements of ions in the atmosphere have been pioneered by F. Eisele. In the simplest of these, a flow of gas at atmospheric pressure is brought into a high voltage drift tube in which the drift direction for the ions of interest opposes the neutral flow direction. The ions are slowed down, extracted from the primary neutral flow, and directed toward a sampling orifice. The ions then enter a high vacuum region of the apparatus and are detected with a pulse counting quadrupole mass spectrometer. The concentrations of the neutrals of interest are calculated from the signals of their product ions generated in reactions with ambient charged species. In a variation of the method, ambient ions are excluded from the flow tube, and specific test ions are injected into the neutral flow to create unique product ions that are detected the same way. Eisele (Georgia Tech and NCAR) is currently under contract to us using FY92 SERDP funds to make initial measurements of ion composition in rocket and jet plumes and will make the first measurements in the spring of 1994. In a collaborative effort closely related to this SERDP proposal, one of the members of our in-house research team is currently investigating the ion chemistry of jet engine plumes at the Max Planck Institute for Atomic Physics in Heidelberg, Germany, under the AFOSR Window-on-Europe program.

Our in-house mass spectrometer development effort will focus on incorporating Eisele's novel chemical ionization techniques into a quadrupole mass spectrometer used for standard measurements of neutral composition at atmospheric pressure. In addition to the ultra-high sensitivity techniques described above, the instrument will also provide variable energy electron impact ionization with differential pumping for detection of the major pollutant species. The portable instrument package will be easily adaptable to field and flight experiments. We have used basic research funding to construct the high vacuum portion of the instrument, containing the mass spectrometer, detectors, differential pumping stages, and electronics and data handling equipment. The sampling flow-drift tube system is currently being designed. SERDP funding will be used primarily to complete the design and assembly of the sampling system, to integrate and test the sampling system, and to make the initial field measurements.

Laboratory measurements of ion chemical rate constants will be made in an existing variable temperature selected ion flow-drift tube (SIFDT), which is the only such instrument available in any DoD laboratory, and in a new high temperature flowing afterglow apparatus, which is the only such instrument anywhere in the world. These types of apparatus have provided most of the previous measurements of the chemical kinetics important in atmospheric ion chemistry. The specific species and reactions to be studied will be chosen after measurements of ion composition in the field are started. We expect that the ion chemistry of trace pollutant species will pose new challenges to the laboratory measurement program. Although the bulk of funding for the laboratory effort is provided by the Air Force Office of Scientific Research, some SERDP funding may be used in future years to develop new laboratory techniques required to make

measurements of specific pollutant species under the extremes of temperature and pressure represented in the actual atmospheric environments.

SERDP funding in FY93 has been used in the laboratory program to develop an ion chemical technique for detection of chlorine nitrate, $ClONO_2$, and to determine the atmospheric lifetimes of perfluorocarbons, which have been proposed as substitutes for ozone depleting chlorofluorocarbons. In a related SBIR Phase II research effort, the heterogeneous decomposition of halocarbons on Al_2O_3 particles from solid fuel rocket engines is being investigated.

The effort proposed here directly supports many of the requirements listed in the Tri-Service Environmental Quality R & D Strategic Plan, including:

Pillar 1, Clean-up: Thrust 1.C: "Characterization/ Monitoring,"
Thrust 1.D: "Chemical Analytical Systems;"
Pillar X: Thrust X.1: "Hazard Assessment;"
Pillar 2, Compliance: Thrust 2.A.2: "Routine Emissions,"
Thrust 2.A.3: "Detection and Monitoring,"
Thrust 2.C: "Manufacturing and Disposal,"
Thrust 2.0: "Compliance Evaluation;"
Pillar 3: Pollution Prevention: Thrust 3.N: "Reduce Greenhouse Gas Emissions."

Our research group has been studying atmospheric ion composition and charged particle chemistry as its core research effort for several years. Applying this experience to specific environmental problems using SERDP funding will therefore be highly leveraged with other funding sources. Specific tasks that will be accomplished with the SERDP funds are:

1) Use existing high sensitivity atmospheric ion detection equipment (Eisele, Georgia Tech, NCAR) to measure ion composition in jet engine exhaust plumes.
2) Develop in-house mass spectrometric capability based on Eisele's techniques; test and calibrate instrumentation in concert with complementary techniques; demonstrate usefulness of technology in field tests using jet engine exhausts, rocket exhausts, and other measurements of opportunity.
3) Perform laboratory measurements of the kinetics of the ion chemistry of trace neutral pollutant species as required to calculate the concentrations of the pollutants measured in the field programs.

8. Expected Payoff:

The Geophysics Directorate of the Phillips Laboratory is an acknowledged world leader in measuring the chemical kinetic properties of ion-molecule, ion-ion, electron-molecule and electron-ion reactions relevant to atmospheric, ionospheric and high temperature plasma processes, and in measuring the ion composition of these environments with mass spectrometers. For this work, our research group was selected to be one of the 1991-1993 Air Force Office of Scientific Research (AFOSR) Star Teams recognizing excellence in basic research relevant to Air Force requirements. The Geophysics Directorate is the only DoD laboratory facility where the in-house expertise in ion chemistry and mass spectrometry can be brought together to develop the high sensitivity trace neutral detection method that we propose.

We plan to focus our efforts initially on the effluents from jet and rocket engine operations in the troposphere and stratosphere. In order to assess the environmental impact of the pollutant

species generated by the combustion process in such engines, the concentrations and lifetimes of the foreign species and the chemistry which they undergo in the atmosphere must be understood. Our proposed research program will lead to high sensitivity measurements of the concentrations of many species in the atmosphere. Models of the chemistry of polluted environments can then be improved by adjusting the model to match the measurements. The validated models can then be applied with confidence to environmental scenarios where direct measurements have not been made and will also lead the way to future research needs. The immediate benefit of the research will be to ensure compliance of jet or rocket engine emissions with mandated standards, to point the way to problems that might cause high emissions, and in general to support DoD efforts to reduce pollution from jet and rocket operations.

In addition, we expect that our ion chemistry technique will be broadly applicable to other requirements for environmental monitoring in the areas of compliance, cleanup, and pollution prevention. We will actively seek opportunities to bring the techniques developed in this research effort to collaborative field campaigns where other complementary trace gas detection techniques are deployed. Comparison and cross-calibration of many techniques will ultimately lead to a battery of instruments which between them can detect pollutant species under more varied environmental conditions than any one technique could alone.

9. Milestones:

1.	Complete test plan for initial jet plume measurements	09/93
2.	Develop ion chemical detection scheme for $ClONO_2$	10/93
3.	Complete first measurements of jet plume composition	04/94
4.	Complete core in-house mass spectrometer	06/94
5.	Integrate flow sampling system into mass spectrometer	06/95
6.	Perform first field-scale demonstration	09/95
7.	Assess technology and commercialization potential	09/96

10. Transition Plan:

The end product of this proposed research will be a portable, highly sensitive, calibrated and tested instrument for determining trace neutral composition in polluted regions of the atmosphere. This product should be suitable for commercialization and sale to the environmental monitoring community, and we will actively seek industry partners interested in developing this technology with us via CRADA agreements or other appropriate vehicles.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	320	500	550	600	600	2570
AFOSR	400	400	400	400	400	2000
TOTAL	720	900	950	1000	1000	4570

12. Performers:

Development of the portable mass spectrometer equipment, measurement of relevant ion chemical kinetics, and analysis of all data will be performed at the Ionospheric Interactions Branch, Geophysics Directorate, Phillips Laboratory, Hanscom AFB, Massachusetts. Georgia Tech and the National Center for Atmospheric Research (NCAR) are under contract to us to make initial measurements of ion composition in jet engine exhaust plumes. The Max Planck Institüt für Kernphysik, Heidelberg, Germany, will be an unfunded collaborator. This effort will be closely coordinated with an associated SERDP proposal, "Rocket Plume Mass Spectroscopic Stratospheric Sampling," in which mass spectroscopic instrumentation will be used on research aircraft to measure rocket plume pollutant species.

13. Principal Investigators:

Dr. John O. Ballenthin and Dr. Albert A. Viggiano
Geophysics Directorate
Phillips Laboratory
PL/GPID, 29 Randolph Road
Hanscom AFB, MA 01731-3010
TEL: (617) 377-4028
FAX: (617) 377-7091

14. Keywords:

ion chemistry, mass spectrometry, airborne pollutants, detection, atmosphere/troposphere/stratosphere, high sensitivity.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Leak Location in Underground Pipelines

3. **Agency:** USEPA

4. **Laboratory:** Risk Reduction Engineering Laboratory

5. **Proposal ID:** #249

6. **Problem Statement:**

The goal of this applied research and technology development effort is to develop and demonstrate a portable and on-line acoustic leak detection/leak location system to accurately and reliably test single and double walled pipelines of various sizes and content (i.e., gasoline, diesel, jet fuel, potable water, low level radioactive wastes, etc.) Such a system would not only assist the regulated community in complying with existing state and Federal regulations but would also reduce the spread of contamination and loss of drinking water through early and more accurate leak detection/location.

Existing Federal regulations (40 CFR Parts 280 and 281, September 1988) require that underground tanks and pressurized pipelines containing petroleum and other hazardous substances be tested for leaks on a regular basis and that once a leak is detected it must be mitigated. This is an onerous task when one considers the enormous number of miles of pipeline associated with retail gasoline service stations nationwide, airport hydrant systems, Army and Navy fueling depots, DOE low level radioactive waste systems, etc. Over 250,000 releases from underground storage systems have been confirmed to date and the EPA estimates that as many as 15 to 20% of the approximately 1.8 million regulated underground systems nationwide either are leaking or are expected to leak in the near future. The environmental threat from these leaking systems has a direct impact on public health because approximately half of the Nation's drinking water supply comes from ground water. Small quantities of gasoline released underground can contaminate millions of gallons of potable ground water with suspected carcinogens such as benzene, etc. The threat is not limited to ground water; leaking petroleum and chemicals can also contaminate surface waters and contribute to air pollution. In addition, these products release vapors that can seep into the sewerage systems of homes and businesses and accumulate to explosive levels. Besides the environmental threats and astronomical costs associated with addressing these threats (over $30.0 billion for site remediation alone) we are also wasting valuable drinking water and energy resources.

Rapid and cost-efficient remediation can occur if the source of an underground leak can be pinpointed quickly and accurately. Current technologies utilizing volumetric- and pressure-based methods are unable to effectively accomplish this objective. Since 1990, EPA's Risk Reduction Engineering Laboratory has been conducting applied research on acoustic technology for rapid, near-real-time leak detection/location in pressurized pipelines typical of those found at retail service stations. Results of this work indicate that acoustic measurements combined with advanced signal processing methods can provide a means by which to detect and locate small leaks over long distances in pressurized pipelines. Additional applied research and technology development work is required to optimize system performance and application on

larger and longer lines and on lines of different configuration. A Science Advisory Board Review (June 1992) of this earlier work (which was funded solely with EPA/ORD funds) recommended continued research in this area.

7. Project Description:

In 1990, EPA's Risk Reduction Engineering Laboratory initiated a program to develop a non-invasive, non-destructive method for detecting and locating small leaks in pressurized pipelines containing petroleum products. Experiments were conducted at the UST/Pipeline Test Facility in Edison, New Jersey in which three acoustic sensors separated by a maximum distance of 125 ft were used to monitor signals produced by 3.0, 1.5, and 1.0 gal/hr leaks in the wall of a 2 inch diameter petroleum pipeline. Line pressures ranged from 10 to 30 psi. Application of a leak location algorithm based upon the technique of coherence function analysis resulted in mean differences between predicted and actual leak locations of approximately 4 inches. This is a significant improvement over current techniques and provides results in a matter of minutes; however, additional experiments with higher pressures and over longer and larger pipelines are required to optimize system performance and expand system application.

The objective of this proposal is to develop, design, fabricate, and demonstrate both a portable and an on-line passive acoustic leak detection/location system that can be used on: (1) existing pipelines, (2) pipeline systems that cannot be breached, (3) newly installed systems, and (4) double-walled pipelines. To meet this objective, a three-phased development and demonstration program will be conducted over a three year period.

Phase I: Modifications to UST/Pipeline Test Facility and Preliminary Experiments

This phase will involve (a) modification of the existing UST pipeline system to make it more representative of systems found at retail service stations, (b) design and installation of a double-walled steel pipeline system typical of DOE systems used to transport low level radioactive wastes, and (c) design and installation of a large diameter (10-12 inches) and longer (300-500 ft.) high pressure pipeline system typical of Army and Navy facilities.

Detailed experiments will be conducted on the representative pipeline systems to determine the accuracy and performance of acoustic technology for locating leaks of differing sizes over variable distances and to identify and evaluate potential differences in performance due to pipeline configuration. Experiments will be designed and conducted to optimize and validate the previously developed "breadboard" system which is based on a coherence function analysis approach; and to evaluate other approaches such as signal attenuation, time of flight, and cross-correlation analysis. The performance of the location system as a function of leak flow rate, line pressure, pipeline diameter, and pipeline length will be determined and validated. Based upon these experiments, recommendations will be made to modify/redesign the existing "breadboard" system.

A protocol appropriate for each pipeline configuration will also be developed for field application of the modified system. The protocol(s) will be based on the current test method which will be refined through selective studies to address questions such as: (a) when testing on longer and wider pipelines, are additional sensors necessary to characterize the signal created by the leak and at what intervals must the sensors be spaced; (b) how will the signal be affected

by leaking valves, changes in pipeline connection hardware, multiple bends and elbows, corrosion anomalies, etc.; and (c) what are the affects of multiple leaks?

Phase II: Prototype Development and Demonstration

Based upon the recommendations of Phase I, a portable acoustic leak detection/location prototype system will be designed and fabricated. The system will enable field testing of pipelines with minimal interruption to commercial operations; most tests will take less than one hour to perform. Using the protocol(s) developed in Phase I, additional "shakedown" testing of the prototype system will be conducted at the UST/Pipeline Test Facility and field validation will be accomplished at actual retail service stations, and Army, Navy, and DOE sites of opportunity.

Phase II will also include initiation of the development of an on-line automatic acoustic system that can be attached to existing pipeline systems or integrated into new systems (single or double-walled) during installation. This would provide constant monitoring with an immediate release detection/location information alarm. System hardware will be developed and preliminary experiments will be conducted on the respective test pipeline systems to identify and evaluate performance characteristics associated with an on-line monitoring system. Recommendations will be provided for prototype design and fabrication, and a protocol will be developed for field application.

Phase III: Final Prototypes and Users Manual

During this phase, final modifications and refinements will be made to the portable acoustic leak detection/location system hardware and software. The system may be further field tested if significant modifications are made and further optimization is required. This effort will result in a user friendly, field applications manual and a final prototype and hardware system (including software) ready for commercial application.

Phase III will also involve fabrication of the on-line prototype leak location/detection system. The system will be evaluated for performance and accuracy on the respective test pipeline configurations. Studies will include signal characterization and algorithm verification. Based on these results, the on-line system software program will be modified and refined. Final field validation of the on-line system will be conducted at new installations or recently upgraded installations (as per the regulations) at DOE, Army, and Navy facilities. The final prototype will then be developed for commercial application.

8. Expected Payoff:

Underground pipelines are used by numerous industries worldwide to transfer liquid products. Presently, only two methods are used to locate leaks in pipelines. The first involves uncovering the line and performing a visual inspection. This is very disruptive to operations, destructive to facility hardware, time consuming and costly. The second method uses a helium or halogen tracer. This technique has serious operational and performance problems, and is also time consuming and costly. Passive acoustic leak detection/location provides an accurate and cost effective workable solution to this problem. Pipelines can be tested in minutes rather than days. Leaks can be located in any line without having to use invasive techniques which are especially costly in low-level radioactive wastelines typically found at DOE facilities. Furthermore, the cost of remediations will diminish significantly as releases are detected earlier and the amount of

excavation associated with a repair is reduced. Most importantly, with more accurate on-line monitoring capabilities, there is better control over product transfer systems, resulting in the prevention of millions of gallons of fuel being released to the environment (and subsequently resulting in the reduction of irreparable damage to our natural resources) and the conservation of a limited energy resource.

9. Milestones:

1.	Complete SOTA review on leak detection for underground storage tank systems	Pre FY94
2.	Design and construct UST/Pipeline Test Facility	Pre FY94
3.	Complete studies of pressure and temperature affects on the performance of leak detection in pipelines	Pre FY94
4.	Complete feasibility study of acoustic leak detection/location technology for pressurized pipelines and develop "breadboard" system	Pre FY94
5.	Modify existing UST/Pipeline Test Facility to represent "typical" (a) retail service stations (b) large diameter/high pressure systems at Army and Navy facilities (c) double-walled systems at DOE facilities	12/94
6.	Complete experimental program on portable acoustic system and develop protocol for field application	03/95
7.	Design and fabricate portable acoustic system and conduct field demonstrations at Army, Navy and DOE facilities	09/95
8.	Final "portable" system prototype and users manual(s)	12/95
9.	Complete experimental program on-line system and develop protocol for field application	09/95
10.	Design and fabricate on-line acoustic system and conduct field demonstrations at Army, Navy and DOE facilities	06/96
11.	Final "on-line" system prototype and users manual(s)	09/96

10. Transition Plan:

Once the technology has been developed, the National Leak Prevention Association, National Leak Detection Association, American Petroleum Institute, National Association of Corrosion Engineers, and the participating agencies in this project will actively market this technology to their constituents. In addition, the EPA will pursue commercialization through the Federal Technology Transfer Act mechanism. There is a great deal of interest in using this technology by the commercial sector due to the tremendous cost savings that may be realized from immediate location of releases, more timely remediations, and conservation of fuel (energy). In addition, the technology has cross-application to pipeline systems involving other contents such as gas, water, sewage, etc.

11. Funding: ($K)

	FY94	FY95	FY96	Total
SERDP	1000	1000	1000	3000
EPA	250	250	250	950
DOE	200	200	200	600
NAVY	150	0	0	150
TOTAL	1600	1450	1450	4700

12. Performers:

This project will be conducted by EPA's Risk Reduction Engineering Laboratory in conjunction with DOE's Oak Ridge National Laboratory, the Naval Facilities Engineering Service Center, Port Hueneme, CA, and the Army Civil Engineering Research Laboratory, Champaign, IL. The project will be coordinated through an Interagency Agreement, whose performers and sponsors will include:

U.S. Environmental Protection Agency: David Ziegle, Director, Office of Underground Storage Tanks, Washington, DC; Anthony N. Tafuri, Robert W. Hillger, Underground Storage, Tank Program, Risk Reduction Engineering Lab, Edison, NJ; U.S. Navy: Elsie L. Munsell, Deputy Assistant Secretary of the Navy, Washington, DC; Ted Zagrobelney, Division Director, Naval Facilities Engineering, Command, Washington, DC; William Powers, Program Manager, Naval Facilities, Engineering Service Center, Port Hueneme, CA; Leslie Karr, Environmental Engineer, Naval Facilities, Engineering Service Center, Port Hueneme, CA; U.S. Army: Dr. Charles Marsh, Materials Engineer, U.S. Army Civil, Engineering Research Laboratory, Champaign, IL; Vincent Hock, Metallurgist, U.S. Army Civil Engineering, Research Laboratory, Champaign, IL; Major Mike McDevitt, Program Manager, U.S. Army Civil Engineering, Research Laboratory, Champaign, IL; U.S. Department of Energy: Sherry Gibson, Program Director, Department of Energy, Washington, DC; Richard Korynta, Program Manager, Oak Ridge National Laboratory, Oak Ridge, TN

13. Principal Investigators:

Anthony N. Tafuri / Robert W. Hillger
U.S. EPA RREL/RCB
2890 Woodbridge Avenue
Edison, New Jersey 08837
Telephone: (908) 321-6604 / (908) 321-6639
Fax: (908) 321-6640

14. Keywords:

Acoustics; Leak Detection; Underground Storage Tanks; Pipelines; Petroleum; Remediation

At the time of printing, a detailed project description had not been received.

Air Quality Monitor

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness

3. **Agency:** U.S. Army

4. **Laboratory:** Construction Engineering Research Laboratories (CERL)

5. **Proposal ID:** #523

6. **Problem Statement:**

Preservation of the Department of Defense (DoD) training, testing and readiness mission requires that DoD be capable of controlling, assessing, managing and monitoring noise problems in the vicinity of its bases and installations. They cannot now consistently do this. The DoD faces continual challenges to planned operations and changes to operations because of negative community responses to the noise created by weapons, helicopters, and aircraft. The direct impact is an insidious loss of training and readiness capability through the closure of ranges and firing points, altered flying, and nighttime curfews. Because of noise, the DoD has lost significant mission capability at over 50 installations. Equally important are delays due to procedural or litigational challenges (as provided for in the National Environmental Policy Act) to environmental impact analysis documents, such as Environmental Assessments (EAs) and Environmental Impact Statements (EISs) that propose changes in DoD operations. Such changes include, for example, introduction of a larger battle tank main gun, introduction of supersonic flying in an area not previously exposed to these operations, changing from an older aircraft or helicopter to a newer one, and increases in nighttime military training. Such challenges are difficult to refute when substantiating information is not available. It is expected that the impacts of environmental noise from military operations will continue to be a significant problem, and with enhanced emphasis on nighttime training, will worsen for the foreseeable future.

DoD needs the ability to predict physical sound levels in the community surrounding an installation due to training activity on post. With such a prediction, training could be conducted at times that are less favorable for sound propagation and thus reduce the community noise exposure. Basic Research is needed to advance our understanding of wave propagation in a turbulent atmospheric (meteorological) medium to augment existing sound prediction tools which currently fail when applied under these conditions.

No present physical models are adequate for predictions in the presence of wind driven turbulence or thermal plumes from solar heating. In these situations, a wave that propagates through atmospheric eddies or thermal drafts experiences refraction and diffraction from its normal path. Predicted focus locations on the ground are moved or diminished and acoustic shadows are insonified via scattering. No theoretical or computational method exists that can simultaneously account for acoustic wave propagation through anisotropic, inhomogeneous, turbulent media (the outdoor air) in proximity with an irregular surface of complex acoustic impedance (the ground).

In terms of human response, the DoD continues to have difficulty meeting NEPA compliance requirements and executing the Air-Installation Compatible Use Zone (AICUZ) and Installation Compatible Use Zone (ICUZ) Programs because there is a lack of adequate scientific data on the effects of environmental noise from DoD operations on the health and welfare of people. The National Environmental Policy Act (NEPA) of 1970 requires federal agencies to predict the expected environmental impacts of their activities.

The DoD requires the ability to assess the combined/cumulative human impacts of joint and/or co-located installations and operations. For example, the DoD has been receiving major challenges to environment impact analysis documents because we do not currently address the combined and cumulative effects of Army and Air Force operations there. Most current community (annoyance) impact assessment methodologies for predicting the effects of aircraft noise on humans rely on annualized average exposure descriptions. These annualized procedures are the day-night A-weighted sound level for fixed-wing aircraft, motor vehicles and most continuous industrial noises, etc. A separate annualized procedure, C-weighted day night average level is applied to blast noise and sonic booms. No method exists to combine these two procedures into one overall assessment. Further, there are serious questions about the efficacy of the current C-weighted procedure for blast and sonic-boom noise. Current methodology combines two categories of noise, blast noise, and sonic boom, together, equally into one assessment. However, the technical basis for this methodology exhibits distinct differences between these categories of sound. Sound character and background ambient present two additional challenges to present assessment methodology.

7. Project Description:

The major purpose of this proposed research and development program is to address the issues described above in a coordinated program involving several major federal agencies including the U.S. Army (USA) and the U.S. Fir Force (USAF), the Department of Transportation (DOT), the Federal Aviation Administration (FAA) and the NASA Langley Research Center. These contacts are documented in the package of coordination letters appended to this proposal. This effort supplements and complements current and planned USA and USAF programs, which only together will provide the funding required to adequately address a series of challenging technical issues. The major focus of this effort is a assessing and mitigating military noise. The combined human effects model is a dose response empirical model that provide the means for DoD to assess and mitigate noise. The propagation research will lead to better analytical physical sound propagation models which will be used to improve the underlying physical predictions of sound for the human effects model. The improved physical prediction model also will be used for direct prediction and warning of high level for noise mitigation purposes. The proposed program is part of the DoD Environmental Quality R&D Plan and is highly rated by the user community. It relates directly to Project Reliance DoD Pillar 2: Compliance (Reliance Sub-area: Noise) and covers several requirements. It addresses several of the Research and Development Objectives of the Compliance Pillar, as listed in the SERDP Strategic Guidance which was provided to prospective proposers to the SERDP program. This program will build on previous research by USA, USAF, FAA, and NASA.

Central to control and management of noise are a set of demonstrated methods to reduce noise. This SERDP program continues the 1993 effort to develop a system to forecast high noise levels and thereby provide for inexpensive noise control at training ranges. Central to assessment and monitoring are the technical capabilities to predict the physical noise environment and the

expected effects of these environments on human populations. In this project, we will attempt to answer basic questions about acoustic wave propagation through turbulent media:

1) Under what circumstances is multiple scattering theory necessary for accurate predictions?
2) How can the statistical moments of the propagated signal be themselves propagated over a ground surface?
3) What is the effect of propagation through a medium where the turbulence distributions are layered?
4) What is the correlation between atmospheric fluctuations and changes in acoustic propagation?

Results from these approaches will be used to seek a valid approximate model for the influence of turbulence on the average propagation, and for statistics of the fluctuating signal, which will incorporate measured values of wind and temperature versus height.

The combined noise model will be developed in three phases. During Phase 1, an initial combined effects model will be developed based on the current sate-of-the-art. This initial model development will be accomplished through working group consensus building using a contract with NAS and ANSI. By 1997, the initial combined noise effects model, developed by consensus by appropriate cognizant bodies, will be completed. During phase 2, the results of other, related RDT&E by the Army, Air Force and NASA and international partners will be used to revise the Phase 1 preliminary combined noise effects model. During Phase 2, new laboratory and field research will focus on specific issues developed by the NAS and ANSI deliberations and the results from other RDT&E. During Phase 3, the combined noise effects model resulting from Phase 2 will be validated in a series of field tests. Traditional community attitudinal survey techniques will be used at a set of sites where combined noise is received. These might include sites near Army installations which include Air Force air-to-ground gunnery ranges such as Ft. Sill or Ft. Drum. Data collection near Navy or Air Force bombing ranges also will be considered. NAS and ANSI will then be asked to review and approve the final, validated combined noise effects mode.

Research on a high-energy impulsive sound effects model (annoyance) will center on two factors (sub-thrusts) which must be better understood in order to reach the overall gaol of a combined noise effects model. For the first sub-thrust, there will be studies to compare and contrast community response to blast noise and sonic boom. Current methodology combines these two categories of noise into one assessment. Laboratory-field studies of these two sounds in the same test will quantify these differences, if any. For the second sub-thrust, there will be studies to better quantify the role of vibration and rattle in response to these sounds. The technical data strongly indicate that vibration and rattle play a major role in large-energy impulsive noise annoyance. However, it is not currently possible to quantify an predict the annoyance generated by these factors in combination with the audible sound.

8. Expected Payoff:

Ultimately, results of this program will be used to decrease loss of military mission operational capability through defending against encroachment and decreasing costs associated with compliance with NEPA requirements. The latter will be accompanied by reducing costs associated with defending planned changes in DoD operations. The payoff will be improved training efficiency and operational force readiness.

The benefit/cost associated with encroachment and compatible land use can be estimated as follows. The Navy has spent over $500M in land purchases through the AICUZ program because of encroachment. A conservative estimate of off-post noise sensitive encroachment growth is 3 acres per day, DoD wide in Zone II and .03 acres per day in Zone III. Conservative estimates of noise-related property devaluation because of noise is 10% in Zone II and 50% in Zone III. This translates to the present value of about $750M at a 7.5% interest rate. Proven noise mitigation techniques are needed to avoid these costs.

Results from the physical model study will be used in computer program for predicting noise levels and in constructing noise contours. These programs, NOISEMAP and BNOISE, are used by the Army Environmental Hygiene Agency to map noise contours for Army installations as apart of the ICUZ and NEPA processes.

The combined human response model will develop improved impact assessment and control methodologies which will be able to deal with the multiple issues and questions raised concerning the current "universal' assessment methodology. This more robust and improved understanding of the issues will manifest itself as increased public acceptance of AICUZ/ICUZ studies and the noise portions of environmental impact analysis documents (EA's, EIS's) for future DoD operations. The results of the proposed program will provide more technically and legally defensible analyses of the effects of noise from DoD operations, less controversy surrounding the issues to be addressed, and less time required to implement changes in DoD operations.

9. Milestones:

Turbulent Boundary Layer Effects on Sound Propagation.

1.	Use perturbations of measured profiles with the FFP	FY93
2.	Study shore range, range dependent media with the PE	FY93
3.	Develop boundary conditions for waves in random media	2Q/FY94
4.	Model and measure spatial and temporal coherence	FY95
5.	Extend coherence predictions to level fluctuation model	FY96

Combined Effects Model for Human Response to Noise

6.	Develop plan for Blast/Sonic Boom Effects Studies	2Q/FY94
7.	Preliminary consensus National Method for Combined Effects	FY97
8.	Validated effects model for high-energy impulsive noise	FY97
9.	Refine combined effects model. NAS issues resolved.	FY99
10.	Test and Validate Revised Combined Effects Model	FY01
11.	Final National Consensus Method for combined Effects Modeling	FY01

10. Transition Plan:

Specific research results that result from this program will be incorporated into the USA AICUZ program and into the FIRE-system which is the primary tool used to mange noise and part RFMSS, the day-to-day Army training range management system. The Army Environmental Hygiene Agency will be the primary Army agency to implement technology transfer. In addition, the primary vehicle to transition the results of the proposed research program to the federal system is through FICON, which was established by direction of Congress for this

purpose in FY92. The primary vehicle to transition to the private sector is through the American National Standards Institute (ANSI).

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	Total
SERDP	550	690	805	720	660	690	4115

12. Performers:

The Department of Defense (DoD) has an coordinated noise program to develop noise mitigation and management technology. The Air Force is responsible for fixed wing aircraft noise and the Army is responsible for artillery and helicopter noise; the Navy relies on the other two services for noise mitigation technology.

The U.S. Army Construction Engineering Research Laboratories (USACERL) will function as the lead laboratory for the physical sound propagation model. Active basic research in this field is done by universities. Penn State, University of Illinois and university of Mississippi publish frequently on topics of this nature. Their work will be integrated into this program. Within the Army, work in sound propagation phenomena is also supported by the Army Tank command and the Army Atmospheric Sciences Laboratory and the US Military Academy, with which we are currently participating with in joint field experiments and in data analysis and theoretical development.

For the Combined Effects Model for Human Response, performing organizations include the USA Construction Engineering Research Laboratories, USAF Armstrong Laboratory, the Federal Aviation Administration, the Department of Transportation, the National Park Service Ranger Activities Division, and NASA Langely Research Center. The U.S. Navy is not an active performer, since they do not actually perform any significant amount of research on the effects of noise on people, however they will participate in the planning and execution of this research. The US Army will be the lead organization.

13. Principal Investigators:

Dr. Paul Schomer and Dr. Michael J. White
U.S. Army Construction Engineering Research Laboratories
2902 Newmark Drive, PO Box 9005
Champaign, IL 61826-9005
Phone: (217) 352-6511
Extensions: Schomer 7229, White 7436
Fax: (217) 373-7251

14. Keywords:

Aircraft, Noise, Impulse Noise, Weapons Noise, Environmental Impact, Annoyance, TES, NEPA, ESA, Endangered, Threatened, Fast Field Program, Rifle Ranges, Small Arms, Noise Abatement, Noise Barriers, Shooting Noise.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Areas:** Compliance

2. **Title:** Characterizing Open Burning/Open Detonation Emissions

3. **Agency:** U.S. Army Dugway Proving Ground (DPG), Dugway, Utah

4. **Laboratory:** DPG

5. **Proposal ID:** #247

6. **Problem Statement:**

The substantial amounts of energetic materials (propellants, explosives, and pyrotechnics (PEP)) accruing within the Department of Defense (DoD) have become an increasing burden on the military logistics system and subject of growing public concern. Storage facilities are now saturated by a demilitarization inventory exceeding 350,000 short tons and huge amounts of additional unwanted munitions are scheduled for retrograding to CONUS from overseas locations. Despite the critical need to reduce the demilitarization inventory, use of the only available process, OB/OD, has been sharply curtailed. Environmental regulators are demanding item-specific empirical data before granting OB/OD permits under subpart X of the Resource Conservation and Recovery Act (RCRA). These data are not available, and the system for obtaining them has not been fully developed. The Department of Energy (DOE) and defense contractors face a parallel situation at their installations which are accumulating substantial quantities of conventional unwanted energetic materials. Until new permits are granted or existing permits extended, the present dangerous situation will continue to worsen. Moreover, an already skeptical public may perceive that the failure of government agencies to obtain new permits as *prima facie* evidence that OB/OD activities are hazardous to their health and to the environment. The U.S. Environmental Protection Agency (USEPA) has begun closing OB/OD operations (e.g., Ellsworth Air Force Base, South Dakota) and citizens are demanding public hearings addressing risks from nearby OB/OD operations (e.g., Camp Edwards, Massachusetts, a field artillery training area for the Massachusetts Army National Guard).

Limited small-scale testing at DPG indicates that OB/OD-generated emissions of interest are so minute that they pose no hazard to health or the environment. However, the facilities, instruments, and procedures used during this previous testing cannot fully address the broad spectrum of conventional energetic materials awaiting disposal.

The goal of this project is to technologically expand testing facilities, instruments, and procedures so that they can be applied to current and projected disposal permitting-data needs. This includes designing new and larger BangBox testing chambers, characterizing emissions of complete munitions, and grouping munitions into emissions families so that future testing requirements can be abbreviated. During the course of this project, the testing system will be refined to the point where it is suitable for technology transfer to the commercial sector and can be marketed worldwide. Research categories include basic and applied research. The project segment characterizing emissions is an exponential technical progression of a previously funded - and significantly smaller - pilot project.

7. Project Description:

The principal investigator (PI) will chair a technical advisory panel (TAP) which includes expert representatives from DoD, the U.S. Environmental Protection Agency (USEPA), DOE, the National Oceanographic and Atmospheric Administration (NOAA), and defense industries, contractors, and national experts. This panel will provide technical direction for this project and serve as a primary means for interagency coordination. Individual panel members will be selected by the PI.

This project will develop the system to sample, identify, and quantify emissions of environmental interest produced by the OB/OD of PEP end items in the DoD inventory, specialty explosives held by DOE, and PEP manufacturing wastes at DoD, DoD-contractor, and commercial sites. Testing will specifically target criteria gases, semivolatile organic compounds (SVOC), volatile organic compounds (VOC), and metals. The pollutant sampling and analysis systems used in the 1993 BangBox testing at DPG will be refined as the pollutants emitted from the various PEP are identified. New sampling and analysis methods (such as across-the-stack monitors) developed by EPA and the regulated community to measure toxic pollutants from stationary sources will be reviewed frequently to determine if one or more of these methods should be evaluated in the BangBox for use with OD and OD. Pollutant measurement systems evaluated in the BangBox found to be applicable to field and BangBox OB/OD activities will be prepared and standard operation procedures as soon as possible. As laboratory and statistical analyses become available, chemical and ammunition experts will group munitions into families by emissions and relate theoretical projections to empirical data so that testing requirements for the demilitarization inventory can be sharply reduced. Project personnel will use the best available technologies including, but not limited to, the enhanced BangBox test facility located at DPG, supercritical fluid chromatography/mass spectrometry, gas chromatography/mass spectrometry, inductively-coupled plasma mass spectrometry, evacuated and passsivated 6-L stainless-steel canisters, and high-volume samplers. The PI, acting in concert with recommendations of the TAP, will direct technological enhancement of these facilities, instruments, and devices as needed. Anticipated detection of most SVOC and VOC emissions will be at the ppt and ng levels, respectively.

This objective also includes design and construction of specialized surface (5000 to 15,000 m^3 with internal support frames and suppressive shields) and ventilated subsurface chambers, the latter having the capability of accommodating the shock, heat, and shrapnel produced by detonating and burning complete munitions containing up to 45 kg of high explosive (HE) material. These specialized BangBoxes will provide the aggregate capability for expeditiously studying the effects of soil type and moisture content, munition and propellant configuration (stacked/unstacked, buried/surface etc), presence or absence of combustion-promoting additives, quantity and type of munitions and propellants, and other variables on the pollutant profile and emission factors resulting from OB/OD operations. They will also provide the means of studying environmental dispersement of SVOCs and metals. If necessary, field OB/OD testing will be conducted in a manner analogous to those executed at DPG in 1990/1991. An integrated database will collect and track data so that the pollution profiles of buried- or surface-detonated tested items can be compared and selected materials studied in more depth to identify the combustion dynamics and the kinetics of the principle chemical pathway associated with the production of pollutants and residues.

A panel of experts in risk assessment will prepare a guidance document listing the most reliable risk factors for the pollutants released from OB/OD activities and specifying how to use BangBox test results with these factors during the permitting process.

This is a low-risk project. All technologies exist, with only a few requiring moderate enhancement before they can be integrated into a complete testing system capable of fully characterizing emissions produced by the OB/OD of complete conventional energetic munition and propellant end items.

Transferring technologies to the private sector for worldwide commercialization is designed into the project. Contractors will conduct most of the technical work, experts from the private sector will be on the TAP, and reports, when security is not a factor, will be in the public domain. Formation of cooperative agreements with private firms as authorized by the Technology Transfer Act will further facilitate transfer of the technology. Proprietary rights of technologies used in execution of this project will not be included in technology transfer agreements without the express consent of the owner(s).

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations.

The primary technical risk of this project is achieving normal combustion processes while also containing emissions during chamber-testing of munitions with an HE content exceeding 10 kg. The critical path encompasses the design and construction of the advanced BangBoxes described above. However, because the existing BangBox at DPG is adequate for testing of complete munitions containing up to 500 g of HE, initial experiments can be conducted with minimal startup time. Development of the risk assessment guidance document is dependent upon completion of OB/OD-related modeling efforts contained in a companion proposal. Testing of combustion-enhancing additives will be dependent upon results of the identifying and preliminary testing of such oxidizers as contained in a companion proposal.

8. Expected Payoff:

This project will provide the emissions data required by Federal and state regulators for evaluating applications for OB/OD permits under provisions of subpart X, RCRA. Existing OB/OD operations should continue and new permits issued if data indicates that risks to health and the environment are negligible. Because OB/OD destruction techniques are the fastest, safest, most understood, and least expensive means of disposing of conventional energetic materials, stockpiles of unwanted PEP items will be rapidly and inexpensively reduced. Funds will not need to be allocated for developing special facilities or item-peculiar equipment for PEP items identified as being suitable for open-air destruction. Conversely, funds can be efficiently directed to development of alternate destruction methods for PEP items found not suitable for open-air destruction. Solid scientific data properly presented should allay existing concerns held by public about the safety of OB/OD disposal operations. Adaptation of the TOF mass spectrometer to BangBox testing of conventional energetic materials should result in a considerable reduction of laboratory assay costs.

9. Milestones:

The following milestone schedule is predicated on DPG receipt of initial funds in June 1994. This schedule contains remaining milestones of the current DPG project sponsored by SERDP,

Advanced Testing of Emissions Produced During Open-Air Destruction of Energetic Materials, which were approved but not included in FY93 funding (indicated by an "*"). The TAP will meet on a quarterly basis unless convened earlier by the PI to address special situations.

1.	First meeting of the TAP	07/94
2*.	Determination of feasibility of grouping munitions by emission families	07/95
3.	Initiate design of one surface and one subsurface BangBox	07/94
4.	First FTTA agreements in place	01/95
5.	Initiate fabrication of BangBoxes	02/95
6*.	Draft report on testing and feasibility	09/95
7.	Surface BangBox completed	11/95
8.	New surface BangBox characterized	12/95
9.	Subsurface BangBox completed	03/96
10.	Initiate experimental testing of five items in new surface BangBox	12/95
11.	Guidance on using risk factors for permit applications released	12/95
12.	Subsurface BangBox characterized	04/96
13.	Initiate experimental testing of five items in subsurface BangBox	05/96
14.	Draft report of first new surface BangBox test completed	12/96
15.	Draft report of first subsurface BangBox test completed	05/97
16.	Twenty technologically different items tested in surface BangBoxes and ten in subsurface BangBoxes and reported each year through FY01	09/01

10. Transition Plan:

The PI will distribute reports containing results of testing PEP items and manufacturing wastes to agencies having responsibility for obtaining subpart X permits and other interested government agencies. These reports will be submitted to the Defense Technical Information Center where authorized members of the private sector may obtain them. The risk assessment guidance document will be distributed to USEPA and state regulatory agencies, and to DoD organizations involved in the permitting process.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	FY01	Total
SERDP	1128	4155	1845	1485	1485	1485	1485	1485	15121

12. Performers:

This project is a collaborative effort. Government agencies involved in this project include the Department of Defense (DPG, Army Environmental Center plus other military departments as munitions are identified for testing), USEPA Atmospheric Research and Exposure Assessment

Laboratory, NOAA, DOE (Sandia National Laboratories), and the private sector (Oregon Graduate Institute of Science and Technology, Alpine West Laboratories, Radian Corporation, ECO LC, Halliburton N.S., and others as TAP requirements expand). This project is part of the SERDP National Program for Open Burning/Open Detonation, for which the U.S. Army is the lead agency.

13. Principal Investigator:

MacDonald Johnson
STEDP-MT-TM-MO
U.S. Army Dugway Proving Ground
Dugway, UT 84022-5000
Tel: (801) 831-5682
Fax: (801) 831-5263

14. Keywords:

OB/OD, BangBox, disposal, RCRA, munition

SERDP FY94 PROPOSAL

1. **SERDP Thrust Areas:** Compliance

2. **Title:** Measuring and Modeling for OB/OD Permitting

3. **Agency:** U.S. Environmental Protection Agency (USEPA), Research Triangle Park

4. **Laboratory:** Atmospheric Research and Exposure Assessment Laboratory

5. **Proposal ID:** #251

6. **Problem Statement:**

The Department of Defense (DoD), Department of Energy (DOE), defense contractors, and commercial firms all face the problem of disposing of unwanted conventional energetic materials. All have traditionally relied upon open burning/open detonation (OB/OD) techniques which, until recently, have kept a potentially dangerous storage situation manageable. In recent years, all have appreciably reduced their OB/OD disposal operations due to provisions of subpart X of Part 264 of the Resource Conservation Recovery Act which requires OB/OD permits which are issued by USEPA regional headquarters.

Permits have not been issued because none of the affected organizations has all the data required to prepare, review, and approve subpart X permits. There are no credible data available concerning the effect that common environmental variables have on the identities and the quantities of the pollutants released from OB/OD activities. Second, none of the atmospheric dispersion models available have been evaluated to determine if they accurately predict or can be modified to accurately predict how the pollutants released by OB/OD activities will disperse in the atmosphere. Third, there are no reliable chemical dispersion models that predict how the most toxic and long-lived pollutants released will distribute between the air, soil, and water at the site. Fourth, most of the air and soil pollutant measurement systems needed to identify, quantify, and track the pollutants released by OB/OD activities have not been validated. Fifth, there is confusion concerning how to assess the risk that the pollutants emitted from OB/OD activities pose to humans.

The lack of progress in issuing permits has caused the general public to regard OB/OD operations as dangerous to both their health and to the environment. This is unfortunate because recent DoD, DOE, and EPA studies strongly indicate that most munitions, propellants, and their manufacturing wastes can likely be destroyed in an environmentally safe manner through OB/OD procedures. Tests conducted at the U.S. Army Dugway Proving Ground (DPG) and at Sandia National Laboratories (SNL) show that small scale detonations and burns conducted in environmental chambers (BangBoxes) can provide pollutant emission factors representative of full-scale OB/OD operations. These tests have identified candidate air and soil pollutant measurement methods which could be useful for monitoring for the pollutants released at OB/OD disposal sites. On the meteorology side, a new generation of ground-based instruments makes possible the measurement of atmospheric conditions up to 2000 m above ground level. Also, SERDP-funded studies being conducted by NOAA staff at the USEPA facilities in Research Triangle Park are providing the fundamental understanding of how plumes diffuse into the convective boundary layer under different meteorological conditions. Since the plumes released by OB/OD operations can reach this boundary layer, an understanding of how

the plume penetrates (diffuses) through this layer is critical to developing reliable atmospheric dispersion models for OB/OD operations.

This project enhances currently-funded DOE, EPA, and NOAA efforts in pollution monitoring and atmospheric dispersion modeling and identifies new efforts in technology demonstration and technology transfer.

7. Project Description:

Due to the close relationship of this project to an OB/OD emissions data acquisition proposal submitted concurrently with this proposal, key members of this project will participate in meetings of the companion project's technical advisory panel. This will facilitate coordination between agencies and departments, and ensure that data acquisition and models are compatible.

This project has four objectives:

The first objective is to develop and validate upper-air meteorological measurement systems. Because the plumes released from OB/OD activities rise quickly, it is important to be able to accurately predict how the pollutants will disperse above ground level. A new generation of instruments will be used to measure, from the ground, continuous profiles of wind, temperature, and some turbulence variables to heights ranging from 100 to 3000 m. An array of these instruments, contained in a mobile platform, will be used in a series of night-time measurements made at about six diverse, non-ideal sites. These should include hillside and hilltop sites in both rolling and quite hilly terrains, shallow and deep valley sites, and sites on inclined tablelands. The mobile instrumentation package will assure uniform quality and completeness of measurements at each site. Instrumentation will include a mini-sodar, radio acoustic sounder, a mini-lidar, a tethersonde with temperature, humidity, wind and turbulence indicators, a portable meteorological mast with several levels of sonic anemometers, microbarographs, and net radiation measurements. These studies will improve our overall understanding of turbulent mixing and provide our first comprehensive understanding of the depth of turbulent mixing at night. They will provide information critical to developing accurate dispersion models for OB/OD permit applications and for identifying the best meteorological situations for conducting such activities.

The second objective is to develop a dispersion model. The dispersion model development part of this project will build on work being done on INPUFF models for EPA by NOAA. An efficient modular puff trajectory model will be developed and validated. The range of applicability will be from tens of meters to several hundred kilometers. Other types of dispersion models may also be examined as the result of the convective boundary layer studies and the upper air measure measurement studies described above.

The third objective is to develop and validate quality assurance and quality control materials and the procedures to use them. These materials/procedures will be needed to document the quality and completeness of the OB/OD test results from the BangBox studies and from open-air OB/OD operations. These materials/procedures will also be needed to quality assure the monitoring data collected during clean-up and closure activities at OB/OD sites. The primary focus will be to develop materials/procedures for semivolatile, volatile organic, and toxic metals.

The fourth objective is to transfer technology. Transferring the technology developed to the private sector for commercialization worldwide is designed into the project since contractors will

conduct most of the technical work and experts from the private sector will be on the advisory panel. The formation of cooperative agreements with private firms as authorized by the Technology Transfer Act will also facilitate the transfer of technology developed during this project.

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations.

This is a low-risk project and no delays or technical impediments are anticipated.

8. Expected Payoff:

This project will allow applicants and Federal and state regulators to evaluate the emissions data obtained to support the permitting process for OB/OD permits under provisions of subpart X, RCRA. It complements development efforts to obtain emissions data from a broad spectrum of conventional energetic materials requiring disposal.

9. Milestones:

The following milestone schedule anticipates receipt of initial funds in June 1994 and is compatible with milestones of the OB/OD emissions data acquisition project.

Upper Air Measurement System	
1. Work initiated	08/94
2. Site selection completed	01/95
3. Mobile instrument package available	06/95
4. Data from first field test available for use in model development	10/95
5. Data from second field site available	03/96
6. SOPs for meteorological equipment available	08/96
7. Data from all (6) field tests available	11/96

Dispersion Model	
1. Work initiated on INPUFF model	07/94
2. Preliminary users' guide available	07/95
3. INPUFF model revised based on user comments and meteorological study results	06/96
4. Model refined, new models validated as warranted by test data through FY01	09/01

QA/QC Materials and Procedures	
1. Work initiated	11/94
2. QA materials for seven SVOCs available	04/95
3. QA materials for seven additional SVOCs available	10/95
4. Methods and guidance updated through FY01	09/01

Technology Transfer	
1. First FTTA agreements in place	01/96
2. Commercialization of technology continues through FY01	09/01

10. Transition Plan:

The PI will distribute reports and model information to agencies having responsibility for requesting or approving subpart X permits and to other interested government agencies. All publications generated by this project will be submitted to the Defense Technical Information Center where they can be obtained by authorized members of the private sector.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	Total
SERDP	350	550	575	250	100	100	100	2025

12. Performers:

This is a collaborative effort. Government agencies involved in this project include the Department of Defense (DPG, Army Environmental Center), USEPA (Atmospheric Research and Exposure Assessment Laboratory, NOAA, DOE (SNL), and the private sector (Halliburton N.S.). Mr Johnson, as the principal investigator (PI) for the R1 SERDP effort at DPG, will take the lead in overall project direction and management. This project is part of the SERDP National Program for Open Burning/Open Detonation, for which the U.S. Army is the lead agency.

13. Principal Investigators:

QA/QC:
William Mitchell
U.S. Environmental Protection Agency, MD77B
Research Triangle Park, NC 27711
Phone: (919) 541-2769
FAX: (919) 541-7953

Dispersion modeling:
William Petersen
National Oceanographic and Atmospheric Administration
c/o USEPA, MD 80
Research Triangle Park, NC 27711
Phone: (919) 541-1376
FAX: (919) 541-1379

14. Keywords:

OB/OD, munitions, pollution, modeling, dispersion

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Hydrothermal Reduction of Energetic Wastes

3. **Agency:** Air Force

4. **Laboratory:** Armstrong Lab, Environics Directorate

5. **Proposal ID:** #180

6. **Problem Statement:**

Goal: The goal of this project is to develop hydrothermal reduction (HTR) as an alternative to chemical hydrolysis for use in systems designed for the safe, nonpolluting disposal of waste solid rocket propellant from manufacture, refurbishment, and demilitarization of large rockets and for disposal of selected Army, Navy, and Air Force conventional munitions. Final treatment of hydrolyzed energetics from the hydrothermal reduction treatment process could then be treated by biodegradation, supercritical water oxidation or advanced oxidation processes. Applications for hydrothermal reduction include treatment of Class 1.1 solid rocket propellant, Explosive D (ammonium picrate), concentrated ammonium perchlorate waste streams and possible recovery of unoxidized aluminum from the ammonium perchlorate contaminated aluminum/binder residue generated in the Class 1.3 propellant ammonium perchlorate recovery process.

This project supports AFMCR 136-5 "Demilitarization/Disposal Requirements Relating to the Design of New or Modification of Ammunition Items" and AFLC SON 003-90 "Solid Rocket Propellant Disposal. Addresses R&DASC001 "Destruction of Chemical Wastes Without High Temperature Incineration", R&DLA0011 "Environmentally Enhanced Solid Rocket Propulsion", and R&DEG004 "Reclamation/Recycling of Munitions".

Targeted department/organization: Activities having responsibility for disposal of waste propellant from rocket motors and energetic waste from demilitarization of conventional weapons. This would include all Tri-Service activities, USADACS, AMCCOM, USN/SSP and the Air Force Material Command, Ballistic Systems Division (BSD) as well as Ogden Air Logistics Center responsible for Air Force large rocket motors. This technology could apply to projects under investigation by the DOE, such as the Waste Component Recycle, Treatment and Disposal Integrated Demonstration and DOE/USAF Pollution Prevention and Waste Minimization Memorandum of Understanding.

Background: Current incineration and open burning/open detonation methods generate air and solid pollution, require permits and site remediation, and are at risk for increased regulation and possible shutdown. The wet air oxidation and supercritical water oxidation operating regions have been explored in other efforts. Supercritical water oxidation of Class 1.1 propellant with chemical hydrolysis pretreatment will be demonstrated at the prototype scale under the Large Rocket Motor Disposal Program. Inclusion of HTR in the program under Pre Planned Product Improvement reduces program risk. Anaerobic biodegradation of ammonium perchlorate is being developed under a related project. These technologies have yet to be demonstrated at the prototype scale. Exploration of HTR provides additional, potentially more economical, treatment options and reduces the overall risk in the development of alternatives to disposal by OB/OD.

Destruction of energetic materials, which are characteristically oxidant rich, in water at temperatures just below the critical point and under reducing conditions (hydrothermal reduction) has received little attention. In a previous 6.2 effort, decomposition of individual energetic materials into smaller, nonenergetic molecules under conditions of hydrothermal reduction was verified in bench scale experiments, and it was discovered that certain salts act as a catalyst or promoter. For example RDX is transformed primarily to formaldehyde, nitrate and ammonium. For energetics containing a strong oxidizer, such as ammonium perchlorate, a reducing agent is added in order to consume the oxidizer.

Energetic feeds to SCWO must be inserted prior to being fed to the reactor. The inserting is accomplished by chemical hydrolysis and, depending on the acid or base used, high salt loadings in excess of that resulting from decomposition of the perchlorate ion will be created. In a SCWO reactor, high temperatures, the perchlorate ion and chloride salts result in corrosion and solids handling difficulties which must be overcome. In HTR, the thermal decomposition into smaller molecules will result in the release of less energy and should allow operations without extensive pretreatment. j Reduction of the perchlorate ion combined with operation at lower temperatures and pressures is expected to reduce corrosion during propellant processing and provides an opportunity to separate the chloride salts. However, corrosion in SCWO is at least partly attributable to chloride salts and lower temperature regions during effluent cooling and similar corrosion may occur in HTR. The effect on corrosion of reducing the perchlorate ion has not been verified experimentally. Preliminary cost estimates indicate disposal of concentrated solutions of ammonium perchlorate by HTR is competitive with biodegradation costs.

Project Status: This program was started using Air Force S&T and FY93 SERDP funds. Continued SERDP funding is required in order to complete the work unit "Validation of Hydrothermal Reduction" which will investigate treatment of solid rocket propellants and for technology scale up/demonstration.

A contract option for investigation of hydrothermal reduction of ammonium picrate is being exercised in Jan 94 with FY93 SERDP funding. Contract award for the project "Validation of Hydrothermal Reduction" is projected in Mar 94 using Air Force S&T funds. A related contract for investigation of hydrothermal reduction of laboratory energetics was awarded in Nov 93 and is fully funded with Air Force S&T funds.

7. Project Description:

Technical Objective: The primary technical objective of this program is to develop hydrothermal reduction for the decomposition of propellant and other energetic materials as an alternative to chemical hydrolysis.

Technical Approach: Bench-scale tests will be run to expand the experimental database. Tests on pure materials will expand the database to higher temperatures, increased concentrations and additional energetic materials including ammonium picrate, and provide a better understanding of catalytic effects. A second set of experiments will test decomposition of propellants and energetic mixtures. HTR of solid energetics formulations will be investigated and the maximum particle size that can be safely treated will be determined. The technology will be advanced from batch experiments to a continuous bench-scale reactor. Preliminary batch scale experiments will determine whether hydrothermal reduction has potential for application to smoke and dyes.

Following completion of the bench scale teste, HTR will be scaled up for demonstration in a 300 gal/day subscale unit. If energetics materials are fed continuously as in a slurry feed, a government owned, subscale SCWO reactor will be refurbished for the demonstration. If the energetics are to be batch fed, as would be the case without size reduction, a new reactor system will have to be built.

Relationship to DoD environmental objectives: Hydrothermal reduction promises a safe, economical nonpolluting method for inclusion in systems designed for disposal of solid rocket propellants and energetic material from conventional munitions. Development of alternatives to open burning/open detonation and incineration are critical if DoD is to fulfill propellant disposal requirements in an environmentally acceptable manner.

Relationship to other work: This effort will exploit other activities focused on the destruction of energetic materials. Removal of Class 1.1 propellant by cryogenic washout and disposal by supercritical water (SCWO) with chemical hydrolysis pretreatment are being demonstrated at prototype scale under contract with General Atomics. Inclusions in the Solid Rocket Motor Propellant Prototype Disposal System, under pre-planned product improvement reduces program risks.

Technical risks: Low to moderate. Reaction paths and the basis for catalytic effects are not well understood at this time. Reduces the overall risk in the development of alternatives to OB/OD.

8. Expected Payoff:

Hydrothermal reduction promises a safe, economical nonpolluting method for inclusion in systems designed for disposal of solid rocket propellants and energetic material from conventional munitions. These systems will provide safe, economical and environmentally acceptable alternatives to open burning/open detonation and incineration for energetics disposal. Hydrothermal reduction can be used as a pretreatment step for supercritical water oxidation replacing other pretreatment options such as acid or base hydrolysis. Hydrothermal reduction may also provide a cost effective method for treating concentrated ammonium perchlorate waste streams and for recovery of aluminum from Class 1.3 propellant waste.

9. Milestones:

Task I. Validation of Hydrothermal Reduction	
Contract for Bench Scale Tests	03/94
Build Continuous Bench Scale Reactor	04/94
Complete Energetic Component Tests	05/95
Complete Tests on Propellants & Mixtures	02/96
Final Technical Report for Bench Scale Tests	03/96

Task II. Hydrothermal Reduction of Ammonium Picrate	
Exercise Contract Option	01/94
Begin Batch Experiments	02/94
Start Continuous Experiments	05/94
Complete Kinetics Studies	02/95
Complete Product Studies	06/95
Final Technical Report	07/95

Task III. Scaleup/Technology Demonstration

Construct Subscale HTR Unit/Refurbish Subscale SCWO Unit	06/95
Install Subscale Unit	09/95
Complete Testing/Demonstration	01/97
Technical Report	03/97

10. Transition Plan:

The technology will be transitioned to AFMC for implementation in propellant disposal. HTR will be included under Pre-Planned Product Improvement for the Solid Rocket Motor Propellant Prototype Disposal System. For application to conventional munitions, smokes and dyes; the technology will be transitioned to the responsible Army, Navy or Air Force organization for implementation.

11. Funding: ($K)

	FY94	FY95	FY96	Total
SERDP	375	750	500	2015
Air Force S&T	385	0	0	908
Total Funds	760	750	500	2933

12. Performers:

SRI International (Menlo Park, CA) will perform work on hydrothermal reduction under a contract to be awarded in Mar 94. The follow on scaleup effort will be performed by another DoD agency or by an outside organization under contract awarded by an appropriate mechanism.

Cooperative/coordinating agencies are; USADACS, USN/SSP, AFMC, OO-ALC, AMCCOM, DOE/OAK RIDGE, DOE/LOS ALAMOS NL, DOE/SANDIA NL, ARPA

13. Principal Investigator:

Capt William Gooden
AL/EQS-OL
139 Barnes Drive - Suite 2
Tyndall AFB, FL 32403-5323
TEL: (904) 283-6239 FAX: (904) 283-6064

14. Keywords:

Near-critical water, subcritical water, hydrothermal reduction, propellant disposal, ammonium perchlorate

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Encapsulation of Hazardous Ions in Smectite Clays

3. **Agency:** DOE

4. **Laboratory:** Argonne National Laboratory

5. **Agency Proposal ID:** #315

6. **Problem Statement:**

The basic initiative under the SERDP Compliance thrust area seeks to develop new and novel materials for the control, treatment, and long term storage of hazardous metal ions, particularly those of toxic heavy metals and radionuclides. This proposal seeks continued funding for the completion of a 3 year program whose first year was supported by the SERDP in FY 1993.

The approach to be used is based on fundamental work on chemically stable organic monolayers at Harvard University and the Weizmann Institute. It involves the long-term encapsulation of ions in a new class of hydrophobic smectite clays, whose properties can be tailored to the specific chemical requirements of a particular hazardous species. Hazardous cations are initially introduced into the matrix of clay minerals, after which the system is encapsulated with hydrophobic agents. Other variations on this theme will also be pursued, including the direct synthesis of hydrophobic clays around a hazardous cation.

Recent research in several laboratories has focused on the use of clays for environmental remediation. Current investigations have sought to develop ways to utilize these materials for the solution of problems in both organic and inorganic environmental contamination. This proposal seeks to combine the results of previous studies with our own expertise in surface modification of inorganic and polymeric substrates to create a new class of materials for use n environmental restoration.

Smectite clays consist of sheets of aluminosilicates which are separated by an interlayer that contains both inorganic cations, such as calcium and potassium, and water molecules. The cations in native clays can be easily replaced by other cations through aqueous ion-exchange processes. Therefore native clays can be readily used as filters for the removal of hazardous heavy metals and radionuclei.

For the remediation of organic materials, clays are traditionally rendered hydrophobic by treatment with quaternary ammonium cations that contain one long chain hydrocarbon tail. The resulting materials have a greater affinity for non-polar and modestly polar organic compounds. This method is, however, inappropriate for hydrophobic encapsulation of hazardous ions. Use of this process after a hazardous metal ion has been exchanged into the interlayer will only result in the release of the harmful species back into the environment. Clays which simultaneously bind hazardous cations and are hydrophobic are, however, of great interest. Such clays should exhibit an increased resistance to leaching of the hazardous ions out of the interlayer by water. They would therefore require less stringent storage conditions once a hazardous material had been placed within them. Alternative methods, ones which do not rely on ion-exchange,

are required to create these desired hydrophobic clays. The development of these methods, and the characterization and testing of the materials which result from them, is the subject of this proposal.

7. Project Description:

We shall begin experimental work on this SERDP-funded activity at the earliest possible date, presumably in November 1993.

The research described in this proposal seeks to replace the traditional cationic methods for creating hydrophobic clays with alterative general approaches which do not require the use of charged hydrophobic species. Specifically, we shall covalently bind alkylsilane groups ($CH_3(CH_2)_nSi$-) to the surface of the clay. This approach therefore will satisfy two simultaneous objectives. First, it will maximize the capacity of the clay for the cation of interest. Since clays are electrically neutral, there is a maximum limit to the number of cations which can reside in the interlayer. By covalently binding the hydrophobic species to the surface, all of the cationic charge within the clay's interlayer is reserved for the cation whose encapsulation is desired. Consequently, the volume required by the storage medium for a given amount of hazardous waste will be minimized. Second, the use of a covalent bond to attach the hydrophobic medium to the clay eliminates the possibility that the modified clay can revert by ionic exchange back to the hydrophilic state. The covalent link between an alkyl chain and the surface of a clay, which is the basis of this proposal, is much more stable to the environment than the coulombic interaction present for the alternative quaternary ammonium species.

The proposed method for creating a hydrophobic clay surface is derived from the work of S.R. Wasserman and G.M. Whitesides on monolayers of alkylsiloxanes. Like quaternary ammonium ions, the silanes change a hydrophilic surface into a hydrophobic one. Unlike the ammonium salts, however, the silanes do not carry a positive charge. They therefore can coexist within a clay along with hazardous cations. both trichloro- ($RSiCL_3$) and trialkoxy-($RSi(OR')_3$) silanes form covalent bonds to the surface by reaction with surface hydroxyl groups. The resultant silicon-oxygen bonds are stable to strong acids, water, and organic solvents. Although this bond is susceptible to strong base, it resists attack under common environmental conditions. Previous work has demonstrated that dense monolayers containing from 2 to 18 atoms per alkyl chain form on surfaces of amorphous silicon oxide. Since clay minerals also possess surface -OH groups, the techniques developed for the creation of monolayers on silica should also be applicable to these aluminosilicates.

The protective layer on the clay will be polymeric. In addition to their reaction with surface -OH groups, the silanes react with surface water molecules, thereby forming silicon-oxygen bonds between adjacent alkylsilanes. The network of siloxane (-Si-O-Si-) bonds which is formed by this process constitutes a stable cross-linked structure that is held in place by bonds to the substrate and to adjacent silanes. This structure is of high molecular density. Well-formed monolayers of alkylsilanes prevent the penetration of even organic species into their structure. Therefore, this type of monolayer is expected to be an effective barrier to the entry of both polar an non-polar solvents into the interlayer of clay that contains a hazardous cation.

The presence of the cations in the interlayer of a clay represents a possible complication for the formation of the alkylsilane structures. The characterization of the cation in the hydrophobic medium will therefore be a major part of this project. In most cases, the positively charged species in a clay's interlayer are surrounded by solvating water molecules. During the

encapsulation process, some of these water molecules may also react with the alkylsilanes. Such a process would further entrap the cation within the hydrophobic structure.

The nature of this project requires a multidisciplinary approach to the creation, characterization, and testing of this new class of clays. The initial focus of the research will be on the determination of the best experimental conditions for the creation of the hydrophobic clays. One crucial question to be answered is whether solution or vapor phase depositions for the silanes are better for this problem. The traditional techniques for the creation of silane monolayers have relied on the use of solution of the silane in organic solvents. However, using gaseous silanes may enable the silane to penetrate further into the interlayer of the clay and form a more extended network of siloxanes. the greater size of the hydrophobic barrier which results from vapor phase depositions may result n a structure which is even more stable to the environment.

Once the clays have been modified, they will be evaluated to determine how successfully the newly created barriers prevent the migration of the hazardous cations out of the interlayer. For these studies environmental stresses, both chemical and physical, will be simulated. Several analytical techniques, including X-ray powder diffraction and atomic absorption, IR, and UV-visible spectroscopies, will be used to characterize the stability of the hydrophobic layer and the changes which the lattice and interlayer of the clay undergo during the simulations. The results of these measurements will characterize how the clays withstand various stresses and how much material leaves the clay and enters surrounding fluids.

Although it is relatively easy to determine what proportion of the cations leach out of the clay, it is more difficult to quantify the penetration of fluids into the interlayer of a hydrophobic clay. Recent work in this laboratory has demonstrated that it is possible to detect by X-ray absorption spectroscopy (XAS) the interaction between transition metal ions and protic solvents as the ion dissolves in the interior of a clay. This new variation on an established technique will be used to evaluate how effectively the modified clays prevent the entrance of fluid into the clay. These experiments will provide complementary information to that gleaned from studies of the composition of the fluids.

Since much of the clay chemistry outlined in this proposal does not depend on the presence of radioactive materials in the clay lattice, most of the studies will use native, ion-exchanged, and silylated clays which contain representative non-radioactive elements, such as the lanthanides. After most of the technical hurdles have been overcome, the final experiments will apply the best modification protocol to more hazardous species.

8. Expected Payoff:

The new and novel clay materials created during this study constitute the development of a new control technology for the treatment and disposal of hazardous wastes. They offer the possibility of improved long term storage for metallic cations whose re-entrance into the environment is undesirable. When native clays are used to filter waste species out of a medium, the resulting immobilized species still require stringent storage. Exposure of such clays to polar solvents which contain other ions can result in the re-exchange of the hazardous waste back into the fluid. Rendering these clays hydrophobic without resorting to charged surfactants will result in materials that are much more resistant to typical environmental stresses. Therefore less rigorous isolation methods will be required for the long-term storage of these hazardous materials.

The modified clays will have a much different affinity for water than unmodified clays and other minerals. This difference should provide an effective means for separation of the hydrophobic materials from native minerals. Should the hydrophobic clays accidentally become remixed with other minerals, re-separation should be simple because of the drastically different flotation properties of the former.

The raw materials for this project, clays and organosilanes, are inexpensive. Clays are a major constituent of the earth, have many industrial uses, and have been proposed for environmental systems where cost minimization is an important consideration. Organosilanes have been used for over three decades for the creation of reverse-phased chromatographic column packings. They are also extremely inexpensive and readily available. Thus novel chemical concepts will be coupled in a rational way to provide a practical solution to a significant environmental problem.

9. Milestones:

1.	Preparation of hydrophobic smectite clays through the use of alkyltrichlorosilanes.	3/94
2.	Preparation of hydrophilic and hydrophobic smectite clays with transition metals in the interlayer.	7/94
3.	Characterization of the native and modified clays using powder diffraction, BET absorption measurements, X-ray photoelectron spectroscopy, flotation characteristics, and other physical techniques as appropriate.	9/94
4.	Synthesis of new organosilanes as required by the results of Tasks 1, 3, and 4.	9/94
5.	Characterization of cations in hydrophobic clays by X-ray Absorption and Anomalous Small Angle X-ray Scattering.	9/95
6.	Evaluation of efficacy of hydrophobic clays in resisting leaching	9/96
7.	Evaluate direct synthesis of clays about hazardous cations.	9/96

10. Transition Plan:

The technology developed under this proposal will be made available to potential users within the Department of Defense and Energy upon successful completion of the study. The creation of hydrophobic clays in bulk will require new, specialized equipment which may be developed under a CRADA agreement. One current supplier of industrial clays, the American Colloid Company of Arlington Heights, IL, has agreed to consult on the creation and use of hydrophobic clays. We shall collaborate with this and other appropriate industrial organization as the scientific and technical breakthroughs develop.

11. Funding: ($K)

	FY94	FY95	Total
SERDP	380	400	780

12. Performers:

The lead organization for this project is the Chemistry Division of Argonne National Laboratory. The principal investigator is a member of the Chemistry Division at ANL. During the testing phase of this program, synchrotron experiments will be performed at the National Synchrotron Light Source and/or the Stanford Synchrotron Radiation Laboratory. The Analytical Chemistry Laboratory of ANL will provide basic analytical services. The analysis of the surface constitution of the modified clays by X-ray Photoelectron Spectroscopy will be performed by an external vender on a cost for service basis. In future stages of this investigation the personnel and the facilities of the Chemical Separation Science and Heavy Elements Coordination Chemistry groups of the Argonne Chemistry Division will help in the preparation and characterization of clays with tracers and other radioactive constituents.

13. Principal Investigator:

Stephen R. Wasserman
Chemistry Division, Building 200
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
TEL: (708) 252-3527
FAX: (708) 252-9288

14. Keywords:

Encapsulation, clays, silanes, monolayers, multilayers, cations

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Kinetics of Supercritical Water Oxidation

3. **Agency:** DOE

4. **Laboratory:** National Laboratories

5. **Proposal ID:** #364

6. **Problem Statement:**

Supercritical water oxidation (SCWO) is an emerging technology under development by government laboratories, universities, and private industry for the treatment of aqueous wastes. It is also suited for treatment of waste materials best handled in water for environmental or safety reasons such as obsolete munitions, rocket motors, and chemical warfare agents. The process is performed at temperatures and pressures above the critical point of water (typically 450-650°C and 240 bar), and is applicable to waste streams containing 0-20 percent organics in water. The effluent from waste processing can be evaluated for compliance with applicable discharge regulations before release, ensuring protection of the environment.

An early patent for the process included data showing 99.99% destruction of many normal and halogenated hydrocarbons including tetrachloroethylene, DDT, and PCB. Since then, the number of organic and inorganic chemicals, as well as complex mixtures, tested by SCWO has grown considerably. However, the application of SCWO to most DoD and DOE waste treatment needs requires that the technology be advanced beyond its current level of development. These improvements will not be possible without better predictive models for the time, temperature, density, and concentration dependence of the oxidation process.

The current understanding of the rates and mechanisms of reactions in supercritical water is limited to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of a predictive model of SCWO. To be generally applicable and valuable as a design too, models must be based on elementary reaction steps or at least a detailed quantitative mechanistic description incorporating all the key fundamental reactions. Valuable progress is being made by several research teams but agreement between elementary models and experiment is only qualitative in most cases. In addition, there is a wide variation in experimental results and model predictions from different research efforts as a function of feed concentration, which emphasizes the need for closer collaboration among researchers.

A thorough understanding of operative chemical kinetics at the level of basic science is required to underpin applications of supercritical water oxidation technology. We propose a basic research project that investigates the currently uncertain chemical kinetics of SCWO. This project is a continuation and expansion of SERDP projects funded FY92 and FY93 title "Kinetic Mechanisms for Supercritical Water Oxidations" which established experimental capability and made initial measurements on fuel species and oxidation products in optically accessible supercritical water oxidation reactors. This project is improving our understanding

of SCWO chemistry by directly measuring the time, temperature, and density dependencies of key reacting chemical species and improving the theoretical basis of reactions mechanistic models. This project extends the scope of the mechanistic models beyond the oxidation of simple single carbon organic systems to larger aromatic species and organic molecules containing nitrogen or chlorine.

7. Project Description:

The goal of this project is to produce predictive chemical reaction models to be sued to aid the design and operation of large scale SCWO equipment. These engineering design models implicitly center on an accurate description of the chemistry of the key oxidation-resistant species. The insight and understanding needed to develop these models will be generated by coupling an extensive experimental program to a parallel theoretical effort producing quantitative mechanistic descriptions of the oxidation processes. These quantitative mechanisms will then be formalized into predictive computer models.

Actual wastes generated at DoD and DOE facilities are complicated formulations of large organic molecules and inorganic compounds such as paints, dyes, bonded explosives, solvents,and oils. However, work at Sandia and elsewhere has indicated that even at mild SCWO operating conditions, feeds of these complicated materials very rapidly convert to mixtures of simple chemicals. These chemicals are oxidation-resistant molecules such as methane and methanol, simple amines and nitrates, and phenol and other small aromatic ring species. Chlorinated systems represent an exceptionally important waste treatment problem for SCWO where hydrolysis and oxidation reactions are closely coupled. The oxidation rates of these molecules are the limiting processes for the complete destruction of complex feed materials.

This research project has several stages defined by the class of molecules to be studied and how these classes fit into a progression from simpler to more difficult chemical systems to model. Following methane and methanol, for which accurate mechanisms should be available from our current studies by late FY94, experiments and model development will be directed at the first two important classes of molecules: simple aromatics characterized by benzene, phenol, and benzoic acid, and chlorinated organics such as methylene chloride and trichloroethylene. The focus during FY95 and FY96 will be to generate accurate predictive oxidation models for engineering design use. Amines and nitrates, an important class of materials that relate to the treatment of energetic munitions and shipboard wastes such as black water, will be addressed in FY96-FY97 after the models for carbon/hydrogen/oxygen systems are in place.

The FY92-FY93 effort established experimental capability at Sandia and made initial in situ measurements on fuel species and oxidation products in optically accessible SCWO reactors. The FY92-FY93 phase also established communication with several university research groups in this field. The work proposed here formalizes the collaborations that have been established with two leading research programs in high-density, high-temperature organic oxidation.

We will be directly collaborating with Princeton University on the chemistry of aromatic compounds and with MIT on the chlorinated and nitrogen containing species. We will work closely with Dr. K.E. Brezinsky and members of his research group at Princeton to develop the mechanistic description of phenol and toluene oxidation under SCWO conditions. We

will collaborate with Prof. J.W. Tester and Co-workers at MIT on experiments and model development for halogenated and nitrogen-containing systems.

The experimental portion of the research entails determining the concentration of reactants, stable intermediates, products, and in some cases radical intermediates associated with the oxidation of simple chemical in supercritical water. The time-temperature-concentration profiles that are measured provide the foundation for the mechanistic description of the many stages that even simple organic molecules pass through to completion of oxidation. Measurements of species concentration profiles of key intermediates are critical to developing chemical mechanisms. The experimental profiles of reactants and products provide test and verification of the quantitative capabilities of the predictive models.

Our work to date has proven spontaneous Raman spectroscopy to be a very useful method for measuring concentrations of a variety of chemical species in supercritical water. We have recorded strong signals from CH_4, CH_3OH, CO_2, CO, H_2, O_2, and N_2 at concentrations below 0.01 mole/liter. Data collected during FY93 on the oxidation of methane have contributed to the understanding of the temperature and concentration dependence of methane oxidation under SCWO conditions. This work demonstrates the power of optical methods for collecting the detailed experimental data that are necessary to completely describe chemical reactivity over wide range of pressure, temperature, and reactant feed concentrations. Measurement of trace species in FY95-FY97 will require application of more sensitive optical methods that will be adapted and applied as a part of this project. The primary experimental difficulty associated with this project is the level of detection sensitivity that will be achievable for reactive intermediates and products of partial oxidation. Consequently, the optical methods will be complemented by the analytical technique of direct sampling and off-line analysis.

The quantitative mechanism and model development will proceed in parallel with the experiments. Initially, predictions from existing elementary reaction mechanisms for low-density, high temperature processes will be compared t results from SCWO experiments. These comparisons will guide the design of new experiments. Subsequently, the results of the experiments will be used to improve the predictive performance of the models. We anticipate that additional steps involving peroxy chemistry will need to be added, as well as high-density corrections to unimolecular rate parameters.

We emphasize that the goal of this project is to produce predictive models for the oxidation of key species in supercritical water and not simply to illustrate the effectiveness of SCWO. The intention is that these models will guide the design of waste treatment equipment for specific DoD and DOE needs and that they will provide the necessary information to overcome critical design issues regarding equipment size, cost, or feed characteristics.

8. Expected Payoff:

Supercritical water oxidation technology is presently in the pilot reactor and production prototype stage at several government laboratories and private industrial facilities. Equipment being fabricated at this stage of technology development uses only the simplest processing concepts and understanding of rate information. For these systems, processing and fabrication costs are small relative to development costs. The next generation of SCWO processing equipment will be at the plant scale and will need to realize significant operational savings relative small scale systems to be viable. In this project, experiments on

mechanisms and rate controlling processes in this unusual environment lead to predictive models for reactor design, predictions of destruction efficiency, and methods for industrial-scale system optimization.

9. Milestones:

1.	Complete experimental studies and model development for methane and methanol at industrial process concentrations.	12/94
2.	Identify hydrolysis role in overall oxidation mechanism for chlorinated organics.	6/95
3.	Complete phenol and higher aromatic experiments.	10/95
4.	Complete mechanism for C,H,O organic oxidation.	12/95
5.	Complete chlorinated organic oxidation experiments.	1/96
6.	Initiate nitrogen-containing species experiments.	1/96
7.	Complete predictive model for C,H,O organic oxidation.	6/96
8.	Complete chlorinated species oxidation predictive model.	10/96
9.	Complete nitrogen dioxide kinetics experiments, model nitrogen and nitrous oxide product distribution.	10/96
10.	Complete amine kinetic experiments, model.	10/97

10. Transition Plan:

Sandia National Laboratories is leading the development of technology for the U.S. Army ARDEC effort in SCWO. A contract is currently being negotiated for the fabrication of an approximately 100 ton/year unit. Results generated from this SERDP project will feed directly and immediately into improvements and modifications of production prototype equipment and larger scale systems designed to treat special munitions waste, pyrotechnics, and other military chemicals. The SCWO research team at SNL works in an environment of open information exchange with research and technology development efforts in universities, industry, and government labs sponsored by the Army Research Office, ARPA, the Naval Civil Engineering Laboratory, and the U.S. Air Force. In addition SNL directly participates in technology development projects in SCWO with the U.S. Army ARDEC, NSWC, and DOE EM-50 Office of Technology Development coordinated through INEL. S.F. Rice serves on the Technical Support Group for the DOE EM-50 project.

11. Funding: ($K)

	FY94	FY95	FY96	Total
SERDP	740	760	790	2290

12. Performers:

The lead organization conducting this research project is Sandia National Laboratories, Combustion Research Department, Org. 8361. Mechanistic development for the aromatic molecules to be studied with FY94 and FY95 funding will be conducted in collaboration with Dr. K.E. Brezinsky and co-workers at Princeton University. Experiments and model development for simple chlorinated species will be conducted in collaboration with Prof. J.W. Tester and co-workers at MIT. In addition to mechanistic theoretical contributions and other collaborative research with Prof. tester and Dr. Brezinsky, this project funds one research associate at MIT, as well as several extended visits to Sandia's Combustion Research Facility by MTI and Princeton researchers to conduct experimental work.

13. Principal Investigator:

Dr. Steven F. Rice
Sandia National Laboratories
P.O. Box 969
MS 9052
Livermore, CA 94551-0969
TEL: (510) 294-1353 FAX: (510) 294-1004

14. Keywords:

oxidation, Raman spectroscopy, kinetics, mechanisms, supercritical fluids, research modeling

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Photocatalytic Process to Treat Pink Water-2

3. **Agency:** DOE

4. **Laboratory:** National Renewable Energy Laboratory (NREL)

5. **Proposal ID:** #349

6. **Problem Statement:**

Goal: Demonstrate a cost effective photocatalytic process that can reduce the level of contaminants in pink water to meet environmental regulations either alone or in combination with a biological or other treatment step.

Targeted Organizations: Military and/or DOE facilities which operate processes that produce pink water.

Research Category: This proposal is for phase 2 of an applied R&D project begun under previous SERDP funding (FY93). It covers the pilot plant phase, design and costing of a full size plant, and technology transfer to Army and DOE munitions facilities.

Background: There is a great need within DOE and DoD for innovative and cost effective technologies that will treat aqueous munitions waste to meet demanding environmental standards. Production lines used to fill ordnance, machine explosives, or decommission devices containing explosives generate large volumes of pink-water- water which is typically contaminated with dilute concentrations of TNT, RDX,HMX, and associated organic compounds (collectively termed nitrobodies). An effective process for destroying nitrobodies in process waste water will eliminate future environmental risks at Army Ammunition Plants.

The conventional method of cleaning pinkwater waste streams and groundwater is to contact it with carbon, which adsorbs the explosive. After three or four use/regeneration cycles the carbon becomes ineffective and must be incinerated. Based on results obtained to date it does not appear that carbon adsorption will be able to reduce nitrobodies to the levels required by new standards for discharge of water.

The proposed work is Phase 2 of a project begun in FY94 under SERDP funding. Phase 1 covers the laboratory work necessary to define and optimize the photocatalytic process for destruction of nitrobodies in pinkwater. Results obtained prior to the start of Phase 1 have established that a novel anaerobic photocatalytic process is more effective in removing nitrobodies from pink water than conventional oxidative conditions. This approach is the subject of a joint Sandia National Laboratories (SNL)/NREL invention disclosure. it has also been found that a combination of this approach with a biological treatment step is very effective in reducing the level of TNT and HMX in pink water. A similar coupling with carbon adsorption will be tested during Phase 1. The results and data from Phase 1 will be

used to design the pilot plant to be operated during Phase 2. Phase 1 includes extensive contacts with DoD sites which will form the basis for the pilot plant site selection process.

Alternative Technologies: A wide range of possible treatment processes have been investigated over the last two decades. Examples include super critical water oxidation, improved carbon and other adsorption processes, ultraviolet (UV/hydrogen peroxide, UV/ozone, and biological methods. However, these processes are projected to be expensive and there are significant questions about performance. The challenge, therefore, is to develop a cost effective process that reduces the concentration of nitro-organic compounds to acceptable levels and does not leave by-products in the water that may be more toxic than the original explosives. This may ultimately dictate a process that is comprised of more than one unit operation for the removal of nitrobodies.

New Program or enhancement: This is the continuation of a SERDP project funded in FY93 but started in FY94. It also would leverage an ongoing program being sponsored by the DOE which is developing solar photochemical technology to destroy other hazardous chemicals in water. The results of the laboratory work now funded in Phase 1 by SERDP will be used as the basis for the design of the pilot plant to be built at an Army site (tbd) in the first part of the Phase 2 work proposed here.

7. Project Description:

Technical objective: The objective is to demonstrate a process that will treat pink water to meet environmental standards that will prevail in the year 2000 and provide the DoD/DOE with performance and cost data that will allow them to make informed decisions about implementation of the process.

Technical Approach: The R&D phase of this project awarded by SERDP in FY93 will result in the optimization of the photocatalytic process for the treatment of pinkwater, an economic analysis evaluating the merits of using either lamps or solar energy as the UV photon source, and a conceptual design for a pilot-scale system. NREL and SNL will use these results to design, construct, and operate a pilot-scale system at a DoD site. The system will be operated over an extended period to collect system performance and operational data.

Task 1. Detailed design- NREL and SNLA will use the conceptual design and experimental data generated from the R&D phase awarded in FY93 to produce a detailed design of a pilot scale system. The system will be used to verify the performance of the photocatalytic process under field conditions. Key issues in this task will include the size of the pilot-scale system, system O&M, and system integration. This task will run concurrently with the selection of a site for operation of the system. The site will be selected from DoD contacts generated during the R&D phase of the project. The Army Environmental Center (AEC) will act as the liaison between the project and the DoD munitions facilities.

Task 2. Construction: Construction of the pilot scale system will include procurement of equipment, fabrication of components and structures, transportation of equipment to the site, site preparation, and installation at the test site.

Task 3. Operation and initial evaluation: The pink water effluent will be closely monitored at this stage to ensure that the system is performing as required to meet water discharge regulations for the site. This task will allow operators to define the operating conditions for

optimum performance in addition to generating early operation and maintenance data. This information will be needed before moving forward to the extended operation and demonstration phase described in Task 4.

Task 4. Modification and extended operation: Information generated in Task 3 will be used to modify the system for extended operation of approximately one year. At this stage, the system will run unattended but will be closely monitored for the duration of the project. Extended operation of the pilot-scale system will generate additional information on catalyst lifetime, performance, and O&M costs and will allow NREL/SNL, and the DoD to evaluate the technical performance and cost-effectiveness of the system.

Task 5. Final conceptual design and cost estimate of a full scale system: A conceptual design will be developed for a system capable of treating the entire pink water effluent at the site. The conceptual design will be in sufficient detail to provide the DoD with a reliable cost estimate based on the performance and O&M data collected from the previous tasks.

Task 6. Technology transfer: This task will be concurrent with tasks 4 and 5. The objective is to communicate the technology to the organizations and plants within DoD and DOE that could use the technology and to facilitate contact between them, companies that can implement the technology, and the SERDP project.

Relationship to DoD/DOE Environmental Objectives: Explosive contaminating water at military facilities is one of the DoD's most serious environmental problems. There are numerous Army munitions facilities in the Untied States that generate process water contaminated with explosives and propellants. AEC's goal is to find a more effective and less costly method than carbon adsorption and incineration for treating pinkwater. By using the photocatalytic process, either alone or in combination with another operation, it may be possible to safely and completely destroy the contaminants in a cost effective manner.

Relationship to other similar ongoing work: The work proposed here will build on the laboratory and small scale field testing of the photocatalytic process and potential companion treatment steps for pink water that was funded by SERDP in FY93. In other interactions; AEC,EPA, and DOE have formed a cooperative Tri-Agency project to demonstrate the use of solar energy to remediate contaminated soil. A system demonstrating the solar concept is planned to be operating at the Sierra Army Depot in California by FY94/FY95. There is no overlap between the technology proposed for the Tri-Agency project and that proposed here for SERDP.

The Department of Energy has a program supporting the development of solar photocatalytic technology to detoxify hazardous organic wastes in water. Laboratory results have been confirmed in a field experiment at a Superfund site in Livermore, California during 1991. A second field experiment was recently completed at the Tyndall Air Force Base in Florida. These results have resulted in substantial industrial interest, and several small companies are currently developing the first commercial systems.

Technical risks: Photocatalytic detoxification of water is based on a body of work in semiconductor photoelectrochemistry that has been developed over the last two decades. It is well established that a wide variety of organic compounds can be completely mineralized (broken into carbon dioxide, water, and mineral acid) in water over semiconductors when they are irradiated with near ultraviolet light. The results of Phase 1 work now underway

will define and optimize the chemistry of the process, select candidate companion treatment steps, provide a cost estimate based on the results of laboratory and limited tests at a DoD site, and serve as the basis for design of the pilot plant to be constructed in the proposed Phase 2. Uncertainties that will be resolved in Phase 2 include questions of scale-up, operation under conditions prevailing at production and decommissioning plants, demonstration of operation on an continuous basis, and the capital and operating cost for projected full scale systems.

8. Expected Payoff:

Benefits: The work proposed here may result in a technology that the Army can use to solve some of its most serious environmental problems at explosive and propellant production and decommissioning facilities. The technology that will be developed will clean process waste water contaminated with explosives. This will eliminate a major environmental threat at Army ammunition plants.

The photocatalytic detoxification process is likely to have application in the treatment of groundwater already contaminated due to past DoD or DOE practices, because the technology can destroy a wide variety of hazardous organic chemicals (solvents, pesticides, and dyes) and also remove heavy metals in water.

9. Milestones:

1.	Start	08/95
2.	Select site for pilot design	01/96
3.	Complete pilot plant operation	03/96
4.	Start pilot plant operation	09/96
5.	Complete pilot plant operation and identify mods	03/97
6.	Complete pilot plant modifications	11/97
7.	Complete extended pilot plant operation	12/98
8.	Design and costing for full scale plant	06/99
9.	Transfer technology to DoD, DOE, and commercial sector	09/00

10. Transition Plan:

Next step: Technology transfer will be a major effort through the duration of the project. The project will result in a new process to treat pink water that is proven by operation of a pilot plant. The information and data will be used as the basis for a conceptual design and cost estimate for a full scale plant that can be built and operated at DoD or DOE sites. This would enable the Army to evaluate the process as an option at its munitions plants.

Coordination: The DOE will be responsible for coordinating the project management with the SERDP program and the AEC. NREL would be the technical coordinator of the project; acting as liaison between laboratory engineers, subcontractors, cooperative research and development agreement (CRADA) partners, and the DOE/Army team. The goal of the DOE in this project is to use photocatalytic technology to solve a problem of interest to the DoD. Achieving this goal requires close cooperation between all of the above mentioned organizations.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	Total
SERDP	0	600	1260	1200	1200	730	250	5340

12. Performers:

DOE: National Renewable Energy Laboratory (NREL), Sandia National Laboratory, Albuquerque (SNL)

DoD: Interactions begun in the first phase of this project with the Army Environmental Center (AEC), and sites generating pink water will be continued and expanded. This will be developed into the selection of a site for the pilot plant. There will be ongoing interaction and technology transfer activities with those parts of the defense industry that require technology to treat pink water.

Industry: Engineering, fabrication, and environmental companies with appropriate experience in the design, construction, and operation of pilot and demonstration plants for process waste treatment will be selected to participate in those phases of the work, through subcontracts, cooperative research and development agreements, and/or other agreement as appropriate to quickly accomplish the work and transfer the technology.

13. Principal Investigators:

Mark Mehos
Daniel Blake
NREL
1617 Cole Boulevard
Golden, CO 80401-3393
TEL: (303) 231-1258 FAX: (303) 231-1331 (Mehos)
TEL: (303) 231-1202 FAX: (303) 231-1995 (Blake)

14. Keywords:

Compliance, Pink water, Treatment, Demonstration, Solar, Photocatalytic

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Waste Forms Based on Separations Media

3. **Agency:** Department of Energy (DOE)

4. **Laboratory:** Pacific Northwest Laboratory

5. **Proposal ID:** #360

6. **Problem Statement:**

A major mission of the DOE complex in general and the Hanford site in particular is the safe disposal of radioactive and mixed wastes. Disposal of such wastes from underground storage tanks will involve partitioning the waste into high-level and low-level components and converting those components into stable solids suitable for long-term storage.

DOE is currently planning to dispose of high-level wastes by converting the most hazardous materials into borosilicate glass. However, existing wastes such as tank sludge contain a range of species including chromates, phosphates, and aluminates which complicate production of borosilicate glass. Given the volume of sludge present (millions of gallons) and the high levels of dilution required to incorporate sludge into glass, it is estimated that direct conversion of existing tank wastes could generate up to 40,000 canisters of high-level waste glass. Not only would such volumes of glass greatly exceed the storage capacity of all known waste repositories, the costs of fabricating the glass alone ($1M/canister) could exceed $50 billion.

In order to minimize both waste volumes and costs, chemical separation procedures are under evaluation to concentrate most of the hazardous species into a small volume of high-level waste, allowing for disposal of the bulk of tank contents as low-level waste materials. An important class of chemical separations involves extracting hazardous species (or species which interfere with glass fabrication) using ion exchange procedures. Unfortunately, the separations process and the ultimate waste disposal process are often treated as separate entities. Commercial ion exchange materials are not tailor-made for hazardous waste disposal, and final waste forms are not being designed based on potential feed-streams generated from different separations scenarios. The focus of this proposal is to integrate separations and high-level waste form processing to optimize waste treatment technologies.

The active element in ion exchange is the sorbent material used to pack the ion exchange column. The sorbent material will ultimately be loaded with hazardous species such as radionuclides. Once the ion exchange column is loaded, two options exist to produce high-level wastes:

(1) The loaded ion exchanger could be used directly as the feed material for producing the final loaded high-level waste. Inorganic ion exchangers, in particular, can be (a) melted with other oxides to form a glass or (b) calcined and sintered to form stable ceramics.

(2) Hazardous species could be eluted from the exchange column and converted into a pure product such as a metal salt. The pure compound would then be converted into a glass or ceramic waste.

Option 1 has the advantage that it minimizes the number of processing steps between ion exchange and final waste disposal. However, Option 1 requires that the ion exchanger itself be compatible with the final glass or ceramic waste form. Option 2 requires more processing, but it relaxes the requirement that the exchanger be compatible with the final waste solid. Option 2 might also generate less high-level waste. Both options need to be evaluated to develop optimum processing schemes for treating hazardous tank wastes.

7. Project Description:

We propose to examine ion exchangers with potential for removing hazardous cationic and anionic species from tank wastes in the context of conversion into final waste forms. Existing candidate materials for Cs+ extraction include: the commercial zeolite IE-96, silicotitanates developed by Bob Dosch at Sandia National Labs, layered zirconium phosphates developed by Professor Abe Clearfield at Texas A&M (and by Allied Signal Corp.), and organic formaldehyde-resorcinol resins developed by Jane Bibler at Savannah River. Inorganic ion exchangers such as layered double hydroxides are under development by the Pacific Northwest Laboratory for removal of anionic species such as the pertechnitate ion. The overall program includes two components:

(1) Synthesis, and/or evaluation of exchangers thought to be effective at removal of species such as Cs^{+}, Sr^{2+}, and TcO_4^{-}. Exchangers will be evaluated for chemical stability, selectivity and ion exchange capacity, and compatibility with existing ion exchange processes. This evaluation will help determine the composition of the loaded exchanger and whether the exchanger is better suited to direct conversion into solid waste or elution to produce a more tractable feed.

(2) Evaluation and development of methods for converting potential feed-stocks produced via ion exchange into solid waste forms. A baseline activity would include determining whether the potential feed is compatible with borosilicate waste glass. However, alternate waste form options will also be explored.

A preliminary analysis of existing Cs+ exchangers illustrates some of the trade-offs associated with selecting materials to be optimized for both ion exchange and waste disposal processes. The zeolite IE-96 can be obtained as pellets suitable for ion exchange applications. IE-96 is also soluble in borosilicate glass. Unfortunately, IE-96 has a low selectivity for Cs+, resulting in low Cs+ loadings and high volumes of exchanged waste. Silicotitanates and zirconium phosphates have excellent selectivities, minimizing the total volume of exchanged high-level waste. Unfortunately, neither material can be used in ion exchange columns since both consist of nanometer-scale particles which can both clog and escape from columns. In addition, neither material is soluble in borosilicate glass. The organic resin has high Cs+ selectivity. However, the material is susceptible to radiation damage, requiring Cs+ elution and conversion before excess damage to the column occurs. As the above examples illustrate, most known exchangers have their own unique strengths and weaknesses for solving tank waste problems. The current program is aimed at identifying and mitigating the weaknesses of each of the above materials to provide the optimum solution to the Cs+ separation problem.

Work performed in the FY93 SERDP program on zirconium phosphate exchangers illustrates the approach we are following to explore processing and waste form options. While zirconium phosphate shows promise as a Cs+ exchanger, the loaded exchanger exhibits a low solubility in normal borosilicate glass due to its high phosphate content. With our SERDP project, we established a collaboration with Professor Delbert Day at the University of Missouri-Rolla to see whether he could develop an alternate host lattice for disposing of zirconium phosphate exchangers. On the SERDP project, Professor Day developed a family of iron phosphate glasses that can be loaded with zirconium phosphate. He was able to show that such a glass can tolerate Cs+ loadings at least as high as 30 wt% (compared with 5 wt% for borosilicate glass) and still exhibit a chemical durability to attack by aqueous solutions exceeding that of both borosilicate waste glass and window glass. The new phosphate glass has potential application for treating eluted cesium salts as well as zirconium phosphate exchangers. In fact, the glasses are under evaluation as a means of converting CsCl capsules (representing 1/3 of the total radioactive inventory on the Hanford site) into a stable glass waste form.

As noted above, several candidate inorganic ion exchangers, including silicotitanates, zirconium phosphates, and layered double hydroxides, have two major problems associated with them: 1) the nanoparticle exchangers must be consolidated or supported in order to be used in ion exchange column applications, and 2) the exchangers have a low solubility in the borosilicate waste glass host. Another activity underway in the SERDP project involves the development of porous glass supports to solve both of the above problems. Professor Day has developed two methods for making porous glass supports for waste disposal applications: 1) leaching of phase separated borosilicate glasses, and 2) sol-gel synthesis of porous zirconium silicate glass. With such synthesis routes, glasses can be prepared with interconnected porosities ranging from micron diameters down to nanometer dimensions. Volume fractions of porosity can be as high as 50%. Such porous glasses could be an ideal support for nanoparticle ion exchangers, which could either be synthesized *in situ* via aqueous precipitation or loaded via colloid chemistry techniques. For certain exchange conditions, silane coupling agents could be used to attach the particles to the support. The supported ion exchanger could be configured as porous fibers or beads for use in ion exchange columns. Once loaded with radionuclides, loaded exchange columns could be hot pressed and/or melted to collapse the porosity in the glass. The resulting waste form would consist of ion exchange particles encapsulated (but not necessarily dissolved) in a highly durable solid glass host. Use of such a composite waste form could reduce waste volumes by as much as a factor of 50 for those exchangers exhibiting poor solubility in current borosilicate glasses. The above technology has yet to be demonstrated, but would be evaluated as part of the SERDP program.

8. Expected Payoff:

As stated above, the fabrication cost per waste glass canister is estimated at near $1M. Any contribution to the processing of hazardous waste that reduces the number of canisters is valuable. The processing issues addressed in this proposal clearly impact the number of waste canisters that must be fabricated. For example, it is estimated that the maximum allowed Ti content for borosilicate glass is 1 wt%. For a typical silicotitanate ion exchanger, this means that the volume of glass required to convert the exchanger into a solid waste for disposal would be roughly fifty times greater than the volume of the exchanger itself. Even if only 100 canister volumes of exchanger were sufficient to treat the 169 million-gallon tanks at Hanford, the process would generate 5,000 canisters of waste glass requiring disposal.

However, if the silicotitanate can be directly converted into a ceramic or encapsulated in a porous glass, only 100-200 waste canisters would be produced for a potential savings to DOE of nearly $5 billion in processing costs alone. The phosphate glasses developed already in the program could have a similar impact on waste volumes if zirconium phosphates are the Cs+ exchangers of choice. An analysis of the different exchanger options might provide different solutions to DOE's waste processing problems than might emerge by consideration of the ion exchange step or glass fabrication step alone. For example, although zeolite exchangers are much less selective than silicotitanates for scavenging Cs+, the zeolites exhibit much higher solubilities in borosilicate glass. Although the zeolite exchanger would produce more solid waste after the exchange loading step, the net solid waste generated as glass canisters could potentially be less for the zeolite if both materials require disposal in borosilicate glass.

9. Milestones:

1.	Complete development of phosphate waste glass	4/94
2.	Prepare porous glass supports for exchangers	9/95
3.	Load and consolidate nanoparticles on supports	9/96
4.	Develop exchanger materials for anion removal	9/97

10. Transition Plan:

The first objective of this project is to provide DOE with a technical basis for making decisions regarding both its separations and waste disposal options. Results from the program will then be implemented and incorporated into the actual tank clean-up procedures. If the program leads to the development of new exchangers, PNL will identify commercial vendors (such as Allied Signal) who will assume production of sufficient quantities to treat all tank wastes. If the major product of the program involves alternate waste forms, PNL will either work to transfer the waste form technology to existing DOE melt facilities, or will work with both DOE and commercial firms to develop alternate waste form fabrication facilities. If the major impact involves process integration, PNL will work closely with personnel assigned to clean-up of the Hanford tanks to see that optimum processes are implemented in a timely fashion.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	Total
SERDP	200	200	175	125	900
DOE	180	220	200	160	900
TOTAL	380	420	375	285	1800

12. Performers:

Organizations performing the work include Pacific Northwest Laboratory (DOE) and the University of Missouri-Rolla.

13. Principal Investigator:

Bruce C. Bunker
Pacific Northwest Laboratory
Mail Stop K2-45
P. O. Box 999
Richland, WA 99352
TEL: (509) 375-5969
FAX: (509) 375-2186

14. Keywords:

Tank wastes, radionuclide separations, ion exchange, glass, ceramics, waste disposal

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Supercritical Water Oxidation of Organic Wastes

3. **Agency:** Navy

4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)
Idaho National Engineering Laboratory (INEL)

5. **Proposal ID:** #035

6. Problem Statement:

The overall goal of this project is to determine if supercritical water oxidation (SCWO) is an effective treatment for certain DOE and DoD organic waste streams.

The DOE has a very large amount of organic wastes, such as cutting oils and solvents, that have been contaminated with radioactive materials. The problem for the DOE is to determine if, through oxidation of the organic portion of the waste into nonhazardous water and carbon dioxide, SCWO can reduce the volume of radioactive material that needs to be stored while separating out the radioactive elements.

The Navy generates about 10,000 tons per year of hazardous organic materials such as waste oils, solvents, cleaners, and paint. It is estimated that Army industrial activities generate about the same amount of organic wastes; Air Force industrial activities generate substantially less. The problem for the DoD is to determine if SCWO is a technically and economically viable method of destroying organic wastes generated by industrial activities. The current disposal cost for these materials ranges from $15 to $45 per gallon of waste. The total cost of organic waste disposal for the Navy was $40 M in 1992. In addition to high disposal costs, the DoD retains legal liability for proper disposal of these wastes.

This effort supports the SERDP goal of effective treatment and disposal of hazardous waste (compliance with the Resource Recovery and Conservation Act).

7. Project Description:

This project will demonstrate, at pilot scale, the use of supercritical water oxidation as a method of destroying organic hazardous wastes generated by DoD industrial activities. In addition, the project will demonstrate the destruction of organics in simulants of wastes generated by the DOE and gain an understanding of the fate of radionuclides in an SCWO system.

In this project, two existing pilot plants of differing reactor designs will be acquired to demonstrate SCWO technology on actual DoD wastes and simulated DOE wastes. These different reactor designs will provide data on two alternative solutions to technical issues related to SCWO system design and operation. This approach will provide the engineering design data required by both DoD and DOE to support the treatment of RCRA wastes on site. The Navy is planning a 6.3A funded onsite demonstration of SCWO technology. The

data produced by tasks 1, 2, and 3 will be used to prepare a detailed specification for the design and demonstration of a SCWO plant to be located at the Naval Public Works Center, San Diego. The tasks comprising the project are:

Task 1: Waste Characterization: Task 1 will produce a detailed survey of the volume, composition, and current disposal costs of organic wastes streams managed by PWC San Diego. Estimates of future volume and composition will also be produced. Split samples of characteristic waste streams will be collected for use in tasks 2 and 3.

Task 2: Data Acquisition (Vessel Reactor). An existing cooperative agreement between DOE and a company called MODAR, Inc. will be used to access an SCWO pilot plant having a vessel type reactor. The MODAR SCWO plant will be demonstrated using selected DoD wastes and simulated DOE wastes. Data will be collected on waste destruction performance, reliability, operability, and plant design problems. This information will provide input for establishing the criteria for the next generation of pilot plant designs and demonstrations.

Task 3: Data Acquisition (Tubular Reactor). An agreement will be established between the Navy and a company that has an SCWO plant having a tubular type reactor for the purpose of conducting comparative performance tests between the two reactor types. The same wastes tested in Task 2 will be tested in the tubular reactor in Task 3. The same data set collected in Task 2 will be collected in Task 3 also in order to provide a basis for comparison between the two reactor designs.

The results of tasks 2 and 3 will provide the DoD and DOE with design information to support onsite SCWO demonstrations. In addition, it is anticipated that new information will be available by the end of 1994 from other research projects currently underway. These projects, supported by DoD, DOE and private industry, will provide additional technical data and engineering solutions to the technical challenges facing SCWO development.

Task 4: Permits, Site Preparation. This effort will gather data on applicable Federal, State, and local health and safety codes, air and water discharge limits, and SCWO operating permit requirements. Site preparation work, such as design of building and utilities modifications, will be initiated.

Task 5: Specification Preparation. This task will develop SCWO performance criteria and prepare contract statements of work for the design, construction, installation, and demonstration of the SCWO plant.

Task 6: Testing of Mineral Acid Forming Wastes: The DOE is designing and fabricating an advanced SCWO reactor that has the potential of eliminating the corrosion problems associated with the processing of halogenated wastes. This task will support testing of halogenated Navy wastes in this advanced reactor.

The critical technical difficulties of SCWO development are associated with materials of construction. More specifically, the major materials problem is the very rapid corrosion of the reaction vessel caused by mixes of strong acids formed when certain types of wastes are oxidized. Also, heating or oxidation of some wastes results in the formation salts and oxides of metals that can adhere to process components and cause plugging of the apparatus. These problems must be solved before an SCWO unit can be designed to treat radioactive materials or industrial wastes such as chlorinated solvents.

This project is directly responsive to DoD and DOE environmental objectives, such as the Army and Navy hazardous waste minimization programs (as expressed in OPNAVINST 5090.1 and similar documents) and DOE's Mixed Waste Integrated Demonstration program.

This project is listed in the Tri-Service Environmental R&D Strategic Plan under pillar 2: Compliance; (Requirement Thrust 2.C.2.a): General Hazardous Waste Management.

This proposed project does not duplicate any current SCWO programs. The Defense Research Projects Agency initiated work in March, 1992 to design, build, test and evaluate a 1500 gal/day SCWO pilot plant to destroy chemical warfare agents. The Air Force initiated work in August, 1992 to develop a 1200 gal/day SCWO pilot plant to destroy the propellants from the third stage motors of Minuteman ICBMs. This joint DoD/DOE project will not include chemical warfare agents, explosives, propellants, pyrotechnic devices, or radioactive materials.

8. Expected Payoff:

It has been demonstrated in a Navy 6.2 project on supercritical water oxidation that SCWO technology can destroy most Navy organic hazardous wastes. Independent economic analyses indicate that the SCWO process will also be economically attractive. Estimated unit disposal cost using SCWO is $10 per gallon, for a savings of $5 to $35 per gallon of waste. The payback period for the capital investment is less than 5 years. There is an estimated DoD market for about 30 SCWO plants of 6000 gal/day total throughput (300 to 900 gal/day of organic material depending on waste composition).

9. Milestones:

1.	Waste Characterization	9/94
2.	Data Acquisition (Vessel Reactor)	4/95
3.	Data Acquisition (Tubular Reactor)	2/95
4.	Permits, Site Preparation completed	9/95
5.	Specifications Prepared	6/95
6.	Testing of Acid Forming Wastes completed	12/95

10. Transition Plan:

It is planned to transition the Navy development of SCWO technology to a field demonstration in FY-95 through the Navy 6.3A Program. The 6.3A program will competitively select the best SCWO technology that is presently available and then design, fabricate, test and evaluate an SCWO plant. It is anticipated that the plant will have the capacity of 3000 to 4000 gallons per day total throughput. The plant will be located at the Naval complex in San Diego, probably at Naval Air Station North Island. Public Works Center personnel will be trained to take over operation of the plant after testing is completed. Detailed design of the plant is anticipated to begin in FY-95, with construction and startup taking place in FY-96.

The user and regulators will be invited to participate at all stages of SCWO pilot plant development to ensure that their concerns regarding safety, cost, compliance, reliability, and other issues are addressed.

11. Funding: ($K)

Table 1 - Funding by Task, including DOE & SERDP funds

1.	Waste Characterization	50
2.	Data Acquisition (Vessel Reactor)	1400
3.	Data Acquisition (Tubular Reactor)	350
4.	Site Preparation	90
5.	Specification Preparation	150
6.	Testing of Acid Forming Wastes	2626
	Total	4664

Table 2

	FY94	FY95	Total
SERDP	364	0	364
DOE	1800	0	1800
TOTAL	2164	0	2164

12. Performers:

DOE: Environmental Restoration and Waste Management (EM-50) (through INEL)
Navy: Naval Facilities Engineering Service Center

The expertise of the chemical process industry will be drawn upon for detailed design and construction of the phase 2 SCWO pilot plant. Opportunities for Cooperative Research and Development Agreements will be pursued when such agreements support the overall goals of this project and do not restrict free and open development of SCWO technology. Specific cooperative development agreements with industry and universities are expected to be identified after initiation of this project.

13. Principal Investigators:

DoD: Mr. Richard E. Kirts
P.E., Pollution Prevention Technology Development Branch
Naval Facilities Engineering Service Center
560 Center Drive
Port Hueneme, CA 93043-4328
Phone: (805) 982-1334 FAX: (805) 982-1409

DOE: Mr. John M. Beller
SCWO Program Coordinator
EG&G Idaho, Inc.
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-3710
Phone: (208) 526-1205 FAX: (208) 526-6802

14. Keywords:

Supercritical Water Oxidation, SCWO, Organic Hazardous Waste, Wet Oxidation, Hydrothermal Oxidation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Shipboard Non-oily Wastewater Treatment System

3. **Agency:** Department of the Navy

4. **Laboratory:** Carderock Division, Naval Surface Warfare Center Annapolis

5. **Proposal ID:** #029

6. Problem Statement:

The goal of this project is to provide DoD vessels with the capability to operate in environmentally sensitive areas by meeting current and future national and international effluent discharge standards.

Provisions of the Clean Water Act control the overboard discharge of untreated blackwater (human waste) and graywater within the contiguous zone of the United States. Implementation of Annex IV of the MARPOL Protocol will regulate the discharge of blackwater and graywater from all ocean-going ships. No proven wastewater treatment technology exists today that will reliably meet both the secondary wastewater treatment standards (total suspended solids ≤ 30 mg/l, biochemical oxygen demand ≤ 30 mg/l, fecal coliform bacteria ≤ 14/100 ml and non-toxic) and the operating requirements of DoD vessels (highly reliable, maintainable, supportable, and safe).

DoD vessels today collect and hold only blackwater in collection, holding, and transfer (CHT) tanks for up to 12 hours, or until tank capacity is reached, while transiting the U.S. 3-mile contiguous zone. Graywater is discharged directly overboard. In the future, the 3 mile limit will probably be extended to 12 miles and graywater discharges may also be regulated. Other nations visited by U.S. naval vessels are also expected to impose more strict environmental laws. Ships that rely on holding tanks will be unable to comply.

This project falls into the technology demonstration category in which the feasibility and cost of combining technologies is demonstrated. A product of this research category is proof of the advantage to be gained through application of new technology.

This project is a continuation of an existing FY93 SERDP project. The FY93 effort involves a laboratory demonstration of complete treatment processes at the bench-scale and a subsequent trade-off analysis. That laboratory work will include pre- and posttreatment schemes coupled with membrane filtration to achieve consistent and acceptable effluent. Results from that evaluation will provide system performance data suitable for scale-up to the shipboard prototype.

7. Project Description:

This project will demonstrate, first pier-side and then aboard ship, a full-scale (approx. 5 gal.-/min) process to treat non-oily wastewater to meet EPA recommended wastewater treatment

standards prior to discharge. The system is a hybrid membrane-based process, combining aeration pretreatment and membrane ultrafiltration.

The prototype will be designed specifically for a test aboard a CHT equipped ship, but will be initially tested pier-side to insure satisfactory process performance prior to shipboard installation. Following the pier-side demonstration, the prototype, less the aeration chamber, will be incorporated into the test chip's CHT system for a performance demonstration.

The proposed process is designed to treat medium and high strength wastewater, primarily of domestic nature. The process incorporates an aeration chamber followed by tubular membrane ultrafilters. Currently 1-inch bore tubular membranes with a 100,000 molecular weight cutoff (MWCO) are recommended. The process is fully automatic and controlled by a microprocessor. Sludge accumulates in the aeration chamber and is withdrawn once or twice per year. Membrane cleaning is required two to three times a year. The membranes are replaced when minimum flux rate cannot be maintained; membrane life of over five years has been achieved in commercial systems. Energy for the system is entirely electrical. The membrane operation accounts for 60% to 70% of the power requirements. The energy cost per 1000 gallons of wastewater is about 50 kWh.

The risks in this project are related to the impact of actual shipboard wastewater on the aeration chamber, membrane life, and membrane cleaning requirements. This project must demonstrate that aeration/membrane filtration technology will work on actual shipboard generated wastewater under actual shipboard generating conditions. The project must also demonstrate an acceptable membrane life under normal operating conditions of at least one year. Evaluation of the process with graywater and non-oily wastewater has been limited to the laboratory. An extended field trial will be critical to verifying process performance with actual shipboard non-oily wastewater. Additionally, synthetic fibers found in the graywater may accumulate in the aeration chamber and eventually present operational difficulties with pumps, valves, and sensors. The aeration chamber is subject to "upset" due to rapid and large changes in feed stream characteristics such as temperature, pH, aggressive chemical oxidants, and salinity. The demonstration will include planned "spiking" of the feed stream to ascertain the impact of these parameters on the system's performance.

A Navy 6.2 Project on membrane technology for graywater treatment identified ultrafiltration (UF) membranes as the central component to the treatment processes. This effort began in FY89 and will complete in FY94. Bench-scale and trial-scale test stands were fabricated for the evaluation of ceramic and polymeric membranes processing graywater under the 6.2 Exploratory Development Program, Block SC2A, P.E. 62233N, RM 33E60, Task F-8. This effort documented the inability of micro- and ultrafiltration membranes alone to treat graywater to meet secondary discharge standards for five day Biochemical oxygen demand (BOD_5). Additionally, it was found that polymeric tubular UF membranes provided the best combination of flux, permeate quality, system simplicity, and reliability in short-term evaluations in the laboratory.

The environmental compliance requirements which are met by this project are identified in the Tri-Service Environmental Quality Strategic Plan as: DoD Pillar 2, Thrust 2.G.2, Non-Oily Waste Emissions from Ships; Requirements 2.II.1.g and 3.II.2.b., Control Blackwater/Graywater from Ships and Integrated Pollution Prevention Systems for Environmentally Sound Ships, respectively.

8. Expected Payoff:

The subsequent advanced development and shipboard evaluation of an Engineering Development Model ensures compliance of every DoD vessel with all current and anticipated graywater and blackwater discharge regulations. Benefits include extended operational time in environmentally sensitive waters, ability to dock in domestic and foreign ports which do not have pier-side waste collection facilities and cost avoidance related to those facilities that do, and a decrease in space and weight on plumbing equipment installations to handle increased graywater holding volume.

9. Milestones:

FY93 Funding		
(9)	Complete contract for the design and fabrication of prototype non-oily wastewater treatment system	05/94
(10)	Complete trade-off analysis of all successful components and down-select	05/94
(11)	Complete laboratory evaluation of treatment process	07/94
(12)	Obligate funds for prototype development contract	07/94
FY94 Funding		
(1)	Select Navy Site for Pier-side Demonstration	10/94
(2)	Complete Preliminary Drawings Package	10/94
(3)	Complete Review of Preliminary Drawing Package	11/94
(4)	Complete First Update of Drawing Package	12/94
(5)	Complete Critical Design Review of First Update	01/95
(6)	Complete Final Update of Drawing Package	02/95
(7)	Complete Fabrication of Prototype	07/95
(8)	Obligate Funds for Analytical Contract	07/95
(9)	Complete Hydraulic Test of Prototype	08/95
(10)	Complete Proof-of-Concept Test at Fabrication Site	08/95
(11)	Deliver Prototype to Navy Site	09/95
(12)	Complete Pier-side Demonstration Test Plan	09/95
FY95 Funding		
(13)	Complete Pier-side Installation of Prototype	10/95
(14)	Complete System Debugging and Initial Testing	11/95
(15)	Complete On-site Assembly of Shipboard Prototype	06/96
(16)	Complete Pier-side Demonstration of Prototype	08/96
FY96 Funding		
(17)	Complete Shipboard System Debugging and Initial Testing	10/96
(18)	Complete Pier-side Demonstration Report	12/96
FY97 Funding		
(19)	Complete Shipboard Demonstration of Prototype	10/97
(20)	De-install Shipboard Prototype	02/98
(21)	Complete Final Report	06/98

10. Transition Plan:

Upon completion of a successful pier-side and shipboard demonstration, the prototype will be transitioned in FY98 to the Naval Sea Systems Command (SEA 03V) Advanced Development Program, P.E. 63721N. That program will design and fabricate engineering development models for evaluation and ultimate acquisition. Adequate industrial production capability currently exists for all components of the proposed treatment process.

11. Funding: ($K)

	FY94	FY95	FY96	F97	Total
SERDP	400	1250	800	400	4175

12. Performers:

NSWC/Annapolis is the lead laboratory on this project. Consultation with the U.S. Army Waterways Experiment Station and members of the Interagency Consortium for Desalination and Membrane Separation Research such as NIST (Chemical Science and Technology Division, Boulder, CO) is planned. A separately funded ONR S&T project to be conducted by the Molecular Biology Program (ONR Code 341) has been proposed and directly supports this SERDP project. That ONR project will investigate methods to enhance the biological pre-treatment process and reduce its susceptibility to wastewater perturbations. NSWC/Annapolis and ONR have collaborated on that project's focus. The universities involved in the ONR project are Purdue University and Clemson University. A contract with Westinghouse, Machine Technology Division, for the design and fabrication of pier-side and shipboard prototypes is planned.

13. Principal Investigator:

John Benson (Code 634)
Naval Surface Warfare Center
Carderock Division Annapolis Detachment
3A Leggett Circle
Annapolis, MD 21402-5067
410-267-2244 FAX 410-267-4874

14. Keywords:

Graywater, Blackwater, Ultrafiltration, Non-oily Wastewater, Wastewater Treatment, Hybrid Wastewater Treatment Processes

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Compliance

2. **Title:** Evaluation of the Use of Waste Energetics as Supplemental Fuels

3. **Agency:** U.S. Army

4. **Laboratory:** U.S. Army Environmental Center

5. **Proposal ID:** #524

6. **Problem Statement:**

The Army, as sole Department of Defense manager for explosives, is currently evaluating and developing safe, environmentally acceptable, alternative disposal and reuse technologies for it's stockpile of waste energetic materials. Waste energetic materials are propellants, explosives, and pyrotechnics and are commonly referred to as PEP. Unserviceable PEP materials are generated from the manufacture of PEP materials, assembly of munitions, and demilitarization of obsolete conventional munitions. It is estimated that approximately 2.5 million pounds of scrap and off-specification energetic are generated each year (1985 estimate). In addition there were an estimated 200,000 short tons of conventional munitions requiring demilitarization in 1990.

The disposal alternatives for these unserviceable PEP materials are open burning/open detonation (OB/OD) and incineration. OB/OD is the preferred method of disposal; however it's use requires a Resource Conservation recovery act (RCRA) Subpart X permit and due to environmental concerns, OB/OD is only allowed on a case by case basis. The Department of Defense (DoD) is seeking to qualify alternatives to OB/OD by 1995 and to adopt environmentally sound practices by the year 2000. Incineration of energetic materials is uneconomical. To safely burn these materials, energetic are mixed with up to 75% water to form an energetic material/water slurry. The water is required to prevent detonation propagation during the material handling and feed process. The addition of water increases the amount of fuel required to incinerate the energetic materials. Neither OB/OD takes advantage of the energy content of these materials.

USAEC, formerly the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), began investigating the feasibility of reusing the energy content from waste energetic materials to produce steam and/or electricity in 1984. Since explosives are a major waste energetic material in the U.S. Army's inventory, the USAEC began investigating the potential of using TNT, RDX, and Composition B as a supplemental fuel.

7. **Project Description:**

The technical objective of this SERDP proposal is continue work on development of the supplemental fuel technology so that it is ready to be transitioned to the installations/users in order to deal with the burgeoning off-specification and obsolete energetic inventory. Continuing to store these obsolete and unstable materials, while awaiting acceptable technical solutions, imposes great safety hazards. Disposal of waste solvated explosives as a supplemental fuel has been successfully demonstrated from the laboratory (1985), to the

bench scale-studies (1988), to the Los-Alamos Pilot-Scale Test (1989), to the conduct of the Hawthorne Pilot-Scale Test (1991). Results of the first pilot scale demonstration at Los Alamos National Laboratory led to a state of-the-art pilot scale system being designed and constructed for mixing solvated explosives with fuel oil and firing the resulting mixture into a standard industrial boiler to generate steam. The test equipment was designed to meet strict safety standards involved in the handling explosives and volatile solvents. The major process equipment items in the pilot scale system are the explosives dissolving system, the fuel explosives blending tank, the boiler and steam vent system, and boiler management system. The boiler selected for the pilot scale system was a standard Cleaver Brooks Model M4000, 2 million BTU/hr, water tube-type boiler which is one tenth the scale of the majority of the boilers used at Army facilities. Although only 5 of the 18 scheduled test trials were completed during the Hawthorne Pilot-Scale test due to the expiration of Weston's contract and due to some operational problems encountered as a result of operating in the extreme cold temperatures of the desert environment (Hawthorne, Nevada) in winter, the technology once again demonstrated the potential to be an effective method to recover energy from waste explosives. Dilute solutions of TNT (1%) were safely and effectively used to supplement No. 2 fuel oil in an industrial boiler and a removal efficiency greater than 99.99% was achieved. Design modifications made to the system in order to overcome operational problems in extreme cold temperature include: compressed air system improved to provide heated and dry air to the diaphragm pump and other air operated equipment; slurry handling piping and blending tank will be heated and insulated to maintain constant temperature during all ambient conditions; instruments measuring level, flow, and temperature of feed blending system have been upgraded; the burners for fuel oil and slurry have been modified to permit separate supply and control of compressed air to burner nozzles; the control system for combustion air modified to respond stack gas oxygen concentration; and the propane pilot burner was replaced with a pilot using compressed air and propane mixing system.

After significant delays at attempting to resume the previously scheduled tests at Hawthorne Army Ammunition Plant, a Memorandum of Agreement between the USAEC and Indian Head Division, Naval Surface Warfare Center (IHDIVNAVSURFWARCEN), Indian Head, MD., was signed in late 1992 to establish a joint service research and development program for the reuse of waste energetics as fuel supplements. The pilot test equipment was moved to IHDIVNAVSURFWARCEN in Jun 93 where the U.S. Army and Navy shall repeat the original 18 test trials, scheduled for the Hawthorne Pilot-Test, to prove out the equipment modifications and to further develop the technology.

The first part of this SERDP project shall be to conduct the 18 test trial with explosives with the upgraded pilot scale test equipment. Three test sequences are planned. Sequence I consists of No. 2 fuel oil only to characterize the boiler combustion characteristics, particularly nitrous oxide emissions at excess air levels ranging from 20% to 30% (without explosives). Sequence II will evaluate No. 2 fuel oil/solvent/TNT and Sequence III will evaluate No. 2 fuel oil/solvent/Composition B. A matrix of explosives concentrations (TNT: 1%, 10%, 15% ; Composition B: 1%, 4%, 8%) and excess air percentages (20%, 25%, 30%) are scheduled. A final report shall be prepared at the conclusion of the testing as well as an operations manual and a video depicting system operation. Equipment modifications shall be made and "as modified drawings" will be prepared (if necessary). A cost analysis shall then be performed and procurement/fabrication shall be prepared.

A Supplemental Fuels Development Support contract which is scheduled to be awarded in Jan 94 shall be conducted in parallel to this SERDP effort. The main tasks under this support contract shall be as follows: identification of nitrous oxide abatement technologies as they probably be required based upon the results of firing a dilute solution (1%) of TNT with fuel oil in Hawthorne Pilot-Scale Test; the contractor (Weston) providing consulting support to IHDIVNAVSURFWARCEN personnel during conduct of the demonstrations defined in this SERDP proposal; identification of acceptable slurry nozzles which van be used for firing propellants/fuel oil slurries in an industrial boiler; to conduct of a comprehensive review of all laboratory and bench scale data pertaining to explosives and propellants-supplemented fuels in order to identify any data gaps existing; and then to develop a test plan and execute testing to answer data gaps identified in order to optimize the development of this technology.

After conclusion of the Pilot-Test with explosives at IHDIVNAVSURFWARCEN and the pilot scale system is readied for the Pilot-Test with Propellants (i.e. slurry nozzle identified in "Supplemental Fuels Development Support" contract is installed, a Pilot-Scale Test with Propellants shall be initiated. Propellants investigated in this Pilot-Test shall be AA2 Double-Base Propellant, Nitroguanidine, Nitrocellulose, and another propellant (to be determined after talks with Holston Army Ammunition Plant). A final report shall be prepared at the conclusion of this testing as well as an operations manual and a video depicting system operation. Equipment modifications shall be made and "as modified drawings" shall be prepared (if necessary). A cost analysis shall then be performed and procurement/fabrication guidance shall be prepared.

The third part of this SERDP project shall be to fund a material handling study at Holston Army Ammunition Plant for their off-specification and scrap explosives and propellants and then to assist them in retrofitting an actual scale boiler for the conduct of an Installation Demonstration.

8. Expected Payoff:

The future implementation of this technology could be a cost- effective disposal alternative to incineration and will become an alternative to OB/OD which soon may not be an option due to the environmental concerns associated with the process. Potential safety hazards may also be mitigated as the large stockpile of these obsolete munitions and scrap and off-specification materials can start to be utilized with this technology for a beneficial end use. This technology will not only benefit the DoD but commercial industry as well.

9. Milestones:

1.	Initiate Pilot Test on Explosives	May 94
2.	Final Report on Pilot Test with Explosives	Sep 94
3.	Cost Analysis/Technology Transfer Package	Mar 95
4.	Finalize Procurement/Fabrication Guidance	Jun 95
5.	Initiate Pilot Test on Propellants	Apr 95
6.	Final Report on Pilot Tests with Propellants	Aug 95
7.	Cost Analysis/Technology Transfer Package	Oct 95
8.	Finalize Procurement/Fabrication Guidance	Jan 96
9.	Initiate Material Handling Study at Holston	Aug 95
10.	Complete Material Handling Study at Holston	Nov 95

11.	Initiate Retrofit of Holston Boiler	Jan 96
12.	Complete Retrofit of Holston Boiler	Jul 96

10. Transition Plan:

DERA funding shall be used to used to fund an Installation Demonstration at Holston Army Ammunition Plant in FY97. The transfer of the technology to the Installation level is described in paragraph 7. Holston Army Ammunition Plant has briefed on this program and has expressed an interest in being the first installation that this technology is transitioned to.

11. Funding: ($K)

	FY94	FY95	FY96	Total
SERDP	800	980	900	2680

12. Performers:

The USAEC and IHDIVNAVSURFWARCEN shall jointly develop and transition this technology (See attached Memorandum of Agreement). Sandia National Laboratories (SNL) as part of the Energetics Material Center (EMC) shall be a partner in this effort as they are investigating, under a separate SERDP proposal, tasks on the removal of energetic material and preparation for conversion which will support the material handling portion of this SERDP proposal at Holston Army Ammunition Plant. SNL as part of EMC also has submitted a SERDP proposal on co-firing with coal or waste-to- energy plants in lieu of fuel oil as in this SERDP proposal and programs can complement one another in characterizing boiler process parameters and in the identification of a suitable off-gas handling system.

13. Principal Investigator:

Louis Kanaras
U.S. Army Environmental Center
SFIM-AEC-TSD/Kanaras (Bldg E4435)
Aberdeen Proving Ground, MD 21010-5401
Phone: (410) 671-1558 DSN 584-1558
Fax: (410) 671-1680 DSN 584-1680

14. Keywords:

Explosives, Propellants, Boiler, Supplemental Fuel, Pollution Prevention, Open Burning/Open Detonation

At the time of printing, a detailed project description had not been received for:

National Environmental Education and Training Center

TABLE A-III FY 1994 CONSERVATION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Community Ecosytem - Management			
Landscape Watershed/Ecosystem Management (A)	1,140	510	A-260
Strategic Natural Resource Management Methodology (DOE)	433	373	A-264
Multiple - Risk/Impact Assessment			
Assessment and Management of Risks to Biodiversity and Habitat (EPA)	1,325	241	A-269
Species/Genetic - Management			
Threatened, Endangered and Sensitive Resources (A)	805	507	A-273
Species/Genetic - Resource Characterization			
Integration of Radiotelemetry, Remote Sensing and GIS (DOE)	0	363	A-277
Fishing Enforcement/Whale Monitoring Using IUSS (N)	3,000	48	A-281
Species/Genetic - Risk/Impact Assessment			
The Effects of Aircraft Overflights on Birds of Prey (AF)	311	89	A-285
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)	800	244	A-288
Genetic Diversity Monitoring in Plants and Wildlife (EPA)	200	246	A-293
Marine Mammal Health Monitoring (N)	250	50	A-297

TABLE A-III FY 1994 CONSERVATION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Watershed/Landscape - Management			
Strategy for Resource Management on DoD/DOE Lands Combined with Decision Support for Disturbed Ecosystem Renewal (DOE)	500	758	A-302
Conservation Total	**8,764**		

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Landscape Watershed/Ecosystem Management

3. **Agency:** Army

4. **Laboratory:** USAEWES

5. **Proposal ID:** #510

6. **Problem Statement:**

Goal: The goal of this proposal is to support the Tri-Services in their efforts to ensure that management of DoD lands provides for: (a) sustained use of natural resources necessary for military requirements; (b) compliance with environmental laws; (c) stewardship of biological, earth, and cultural resources; and (d) continued overall leadership in natural and cultural resources management.

Problem: The numerous and complex interactions among biological, earth and cultural resources require an interdisciplinary approach for management and dictate the need for a holistic approach to characterization and management of these resources. To achieve the most effective stewardship of biological, earth, and cultural resources, DoD land managers (i.e., Training Area Managers and Resources Managers) need to focus on the landscape level watershed/ecosystem (LWEM) approach to management. This approach is based on defining an area of interest, such as a watershed, in which functional interrelationships of ecological components can be identified and managed to the benefit of the overall watershed ecosystem. LWEM provides a context for better localized management, such as in the case of DoD holdings within a watershed. Information on existing techniques for the LWEM approach to management is scattered among various data sources and is not readily available to installation land managers. Existing supporting information needs to be identified, evaluated, field tested, and compiled into easily accessible and usable forms. Because the landscape approach is still a developing arena, there are gaps in the information needed to link the more conventional resources-specific management into one comprehensive LWEM management scheme. Researchers need to focus on these needs and provide installation managers with complete, practicable, and effective tools to accomplish landscape level biological, earth, and cultural resources management.

Project Objectives: The objectives of this project are to: (a) provide DoD land managers with tools and techniques that will facilitate the LWEM approach to land use planning and management; (b) provide for defensible evaluation of impact due to human activities; and (c) provide for defensible predictions about how proposed use may sustain or alter important biological, earth and cultural resources.

Research Category: This project will include basic and applied research, and technology transfer.

Status: This is a new programmatic proposal.

7. Project Description:

Technical Objectives: The technical objectives of this project are to: (a) identify and evaluate existing techniques for LWEM biological, earth, and cultural resources management; (b) identify/develop information and techniques to close gaps that exist in LWEM guidance; (c) develop LWEM models and knowledge-based systems that can be integrated with visualization techniques and that field managers can run on a desktop computer, and (d) conduct workshops for information transfer on technologies identified or developed under this research effort. The project embraces research in support of LWEM for the full spectrum of biological, earth and cultural resources on DoD lands.

User Requirements: This research will support all of the SERDP Conservation Thrust Area objectives, especially the objective to, "Develop and demonstrate efficient techniques to maximize use of military lands with minimal impact to natural resources in a manner consistent with the Services' mission and Federal environmental regulations." This research will also support the Conservation Pillar Thrust Areas in the Tri-Service Environmental Quality R&D Strategic Plan (Green Book).

Approach: This is a programmatic proposal that provides a research shell and pathway for support of LWEM. A team of scientists from USAEWES, USACERL, USACRREL, USATEC and ERDEC will: (a) coordinate and integrate into the LWEM concept research associated with the six technical milestones listed under paragraph nine of this proposal, and (b) evaluate existing LWEM tools and techniques from the perspective of DoD needs. In addition, strategies will be developed for: (a) accomplishing research required to close some of the gaps in resources information and techniques needed to support LWEM on DoD lands; (b) integrating techniques and information from multiple fields of study; (c) developing models and knowledge-based systems to help guide LWEM decisions, (d) developing a synthesis report (manual) that provides generic guidance (strategies and protocols) on LWEM; and (e) conducting technology transfer.

To the extent that SERDP funding and leveraged funding will permit, research work units will address facets of the following general topics from the LWEM perspective:

Topic 1. Identification of basic and synergistic [i.e., co-dependent] ecological processes and functions.

Topic 2. Inventory and evaluation of biological, earth, and cultural resources, and monitoring of trends in the quantity and quality of these resources.

Topic 3. Assessment and management of impacts of both the forces of nature and military activities on resources.

Topic 4. Avoidance or minimization of impacts of military activities, including protection of unique or sensitive resources.

Topic 5. Restoration or mitigation of degraded resources.

A critical step in this project is the merging of pertinent resources information into strategies and protocols for implementing LWEM on DoD lands.

8. Expected Payoff:

This research project will provide tools to support (a) defensible decisions relative to land allocation for military use, (b) actions needed to comply with environmental laws, and (c) strengthened biological, earth and cultural resources stewardship. The products will be applicable to all DoD installations in the U.S. with land management responsibilities. This research will integrate results and products from SERDP programs in threatened, endangered and sensitive resources, and biodiversity, and from U.S. Army civil works R&D programs.

9. Milestones:

1. Phased Array Ultrasonic Detection of Artifacts (Topic 2):
   - Survey commercial systems and services 06/95
   - Develop control and imaging software 09/96

2. Terrain modeling and Soil Erosion Simulation (Topic 3):
   - Incorporation of erosion/sediment control practices into models with the tools for assessment of their effectiveness 09/96

3. Advanced Biotelemetry for Resource Management (Topic 4) 09/97

4. Sustainable Use/Carrying Capacity Analyses for Military Lands (Topic 2):
   - Conduct workshop to transfer current technology on sustainable use analyses 09/97

5. Stabilization of high Use Training Areas (Topic 2):
   - Complete collection of plant clones and seeds for selected training areas 09/97
   - Determine performance of new cultivars 09/99

6. Development of overall Management Strategies for the Reduction of Noxious Plants (Topic 3) 09/99

Programmatic Milestones

1. Establish team of R&D and installation personnel to identify initial strategies and protocols for implementing LWEM on DoD administered lands 09/96

2. Evaluate existing tools/techniques and identify needed tools/techniques for LWEM 09/97

10. Transition Plan:

The technology developed through this research effort will be transferred through: (a) handbooks, (b) manuals, (c) software for LWEM knowledge-based systems, (d) demonstrations of use of the handbooks, manuals and knowledge-based systems at military installations, and (e) technology transfer workshops for installation land managers. The research team will address data compatibility among researchers early in each facet of research. The feasibility of using videos and computer aided learning techniques for technology transfer will be evaluated as the project moves forward. Journal publications will be encouraged to increase awareness of DoD stewardship leadership in the scientific community. Data bases, tools and techniques

developed in this research will be incorporated into the ITAM program. The research team will be alert for and will pursue CRADA opportunities.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	FY01	TOTAL
SERDP	1140	1780	2700	1200	950	875	000	000	8645

12. Performers:

The principal performers in this research effort will be the scientists of USAEWES, USACERL, USACRREL, USATEC and ERDEC. These scientists will coordinate and, when possible, partner activities with Tri-Service installation personnel, with land management agencies such as USFWS, USDA FS, USDA SCS, BLM, and BUREC, with academia, and with the Nature Conservancy and other conservation organizations.

13. Principal Investigators:

Dr. C. J. Kirby
USAEWES-ER
3309 Halls Ferry Road
Vicksburg, MS 39180
Phone: 601-634-3456
Fax: 601-634-4016

Dr. William Severinghaus
USACERL
P.O. Box 9005
Champaign, IL 61826-9005
Phone: 217-398-5483
Fax: 217-398-5470

Dr. William S. Seegar
ERDEC
Aberdeen Proving Ground, MD 21010-5423
Phone: 410-671-2586
Fax: 410-671-5292

Mr. Antonio Palazzo
USACRREL
72 Lyme Road
Hanover, NH 03755-1290
Phone: 603-646-4374
Fax: 603-646-4561

Mr. John Anderson
Research Institute
USACETEC
Cude Building #2592
Fort Belvoir, VA 22060-5546
Phone: 703-355-3203
Fax: 703-355-3176

14. Keywords:

Landscape Planning, Watershed Management, Ecosystem Management, Ecosystem Functions, Integrated Resources Management, Cultural Resources, Natural Resources.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Strategic Natural Resources Management Methodology

3. **Agency:** DOE

4. **Laboratory:** Argonne National Laboratory (ANL)

5. **Proposal ID:** #373

6. **Problem Statement:**

Argonne National Laboratory (ANL), in conjunction with the U.S. Army Corps of Engineers, Construction Engineering Research Laboratories (USACERL), proposes to develop a Strategic Natural Resources Management (SNRM) methodology that will meet the planning needs for biological conservation and resource management on military installations and Department of Energy (DOE) sites. This proposed methodology will allow land-use conflicts to be identified and optimally resolved and will determine least-cost solutions to long-term land stewardship issues. This approach will quickly provide pertinent information for determining, evaluating, and resolving natural resource/land-use conflicts, as well as for long-term planning and management of these natural and cultural resources.

The proposed project offers a technology that enables resource managers responsible for public lands to identify and analyze competing and complementary land uses and incorporate least-cost, optimization, and "what if" scenarios into their decision-making. The initial emphasis focuses on Army installations; however, the technology will be a tool relevant to the needs of the Navy and Air Force, the Department of Energy, such agencies as the Bureau of Land Management and the National Park Service, and other federal and state land managing agencies. As such, SNRM is a dual-use technology with the potential for leveraging Department of Defense funds with those of other agencies for future enhancements and technology transfer.

Background work underpinning this proposal was conducted by ANL at Fort Riley, Kansas, where ANL has developed a dynamic community landscape model that will link the installation's training mission with the protection of its natural and cultural resources. The model is being integrated with a rule-based expert system and geographic information system (GIS) to create a user-friendly interface to be used by the installation's natural resources planning staff. The proposed SNRM methodology will expand and generalize the Fort Riley model to meet the major needs of biological conservation and resource management on military installations and Department of Energy sites.

Relevant USACERL projects have been funded through the Legacy Resource Management Program to develop pilot computer technologies to assist in integrated natural and cultural resource planning and management on military installations. These USACERL projects include XCRIS, an X-windows-based Cultural Resource Information System, and GRASS-PRISM (Planning and Resource Integration Stewardship Modules). These efforts have linked computer tools, including GRASS as a GIS, a relational database management system, and graphic user-interfaces using Xgen for easy-to-use information access and decision support technology. Initial resource "modules" include cultural resources and historic preservation, forestry, endangered

species (specifically for the red cockaded woodpecker), and watershed management and erosion control. The SNRM technology will build upon these efforts by developing a quantitative approach to evaluating land-use alternatives and long-term resource management scenarios.

7. Project Description:

The content of this project addresses several thrusts within the Conservation Pillar of the Tri-Services Reliance R & D Strategic Plan (green book), including Thrust 4A: Natural and Cultural Resource Data Integration and Reporting; Thrust 4B: Range/Training Carrying Capacity; Thrust 4D: Land Management and Scheduling; Thrust 4I: Range/Training Area Revegetation; and Thrust 4K: Sensitive Ecosystem Management.

7.1 Vegetation Dynamics Model: The basis for modeling changes in vegetation is the vital attributes scheme of Noble and Slatyer, which classifies vegetation physiognomically based on its response to different types of disturbance. For example, species respond differently to such disturbances as flooding, fire, trampling, etc. Different vegetation types and successional stages are identified, and a matrix is then developed showing the transition times for natural succession and for responses to disturbance. This matrix identifies the consequences of all possible management actions or disturbances, such as fire, tree planting, fertilization, and tracked-vehicle activity, in terms of changes in vegetation type. This approach allows multiple, spatially distributed disturbances and management activities to be evaluated in terms of their short-term and long-term effects on the vegetation and the landscape. It also allows recovery from disturbance to be modeled.

7.2 Spatial Analysis: In SNRM, GIS is used for far more than mapping alone. First, the interaction between the locations of management actions and their effect on vegetation is explicitly modeled in the GIS, with the GIS acting as the database to store and update vegetation-type changes on a spatial basis. Second, some components of change are modeled in the GIS in an explicitly spatial manner. For example, at Fort Riley, forest has spread rapidly on newly acquired land, but all new forest adjoins existing forest and most occurs in stream valleys. The process of forest spread is being modeled with a spatial contagion model. Other such spatially explicit processes include fire spread and training damage.

7.3 Biodiversity: A basic problem with the current concept of biodiversity has been that an operational definition does not exist by which biodiversity or habitat integrity may be quantified. A new technique developed at ANL (Loehle and Wein, 1993, Ecol. Mod.) provides such a definition at the landscape scale, based on the similarity of different plant communities and their spatial arrangement on the landscape. This technique can quantify not only habitat fragmentation (e.g., due to roads) but also the cumulative effects of disturbance on vegetation structure. This approach will be integrated into the GIS as part of the work proposed for funding under SERDP. The U.S. Fish and Wildlife Service and National Biological Survey are developing guidelines for approaches to biodiversity, which we will also incorporate as needed.

7.4 Optimality Analyses: Using the vegetation change, spatial analysis, and biodiversity components, the core analysis can then be conducted using optimization approaches. First, the utility function must be defined. This function represents the overall level of management satisfaction that would result from various levels of grassland dominance of the land base. For example, at Fort Riley, Kansas, a simple utility function is

$$F = w_1 xTV + w_2 xGV + w_3 xWHV$$

where x = acres of grassland (% of area), TV = Training Value function, GV = Grassland Value function, and WHV = Wildlife Habitat Value function. The weighing w values represent the relative importance of the different goals. Training value for vehicle maneuvers is maximal at about 80% grassland and declines above and below this value. Grassland value increases as degree of nativeness of the grassland increases. Wildlife habitat value is based on key game species' habitat requirements. More complete utility functions for Fort Riley are under development, but this illustrates the general concept.

Given a utility function, the feasible management alternatives are determined that will allow the closest possible achievement of the optimal outcome. By introducing cost of management activities, the least-cost management scenario can be generated. The SNRM methodology generates scenarios that are less likely to incur future ecosystem rehabilitation costs. Thus, stewardship issues are inherently incorporated into the framework.

7.5 Project Tasks: The major objective of this proposal is to expand, refine, and integrate the current dynamic landscape community model being developed for Fort Riley into a more generally useful SNRM system for all military installations. The three major tasks to be undertaken are to (1) model vegetation classes and dynamics, (2) develop utility functions for various landcover configurations, and (3) incorporate appropriate optimization procedures into the SNRM system.

The central functional component of the SNRM system is a model of vegetation (land-use) change, which incorporates both endogenous changes and those resulting from management activities. For the purposes of land management at military bases, it is not necessary to model the fate of every vegetation type, but merely the basic physiognomic classes (forest, grassland, wetland). A basic framework of vegetation types and their transitions will be worked out for SNRM that will apply to most military bases and DOE sites.

The second type of transition is that resulting from management actions. For SNRM, a complete list of possible (feasible) management actions and their effects will be compiled, along with their costs. Included in this list will be costs for complete rehabilitation actions, such as restoration of a severely eroded hillslope or wetland.

In order to evaluate tradeoffs in land use and conservation, utility functions are needed. First, the utility functions defining the utility of different land cover configurations for various management purposes (e.g., training) are needed. USACERL will help define these utility functions. Second, costs are included as a function to be minimized. This helps guide the selection of management scenarios away from those that lead to severe site degradation, with their concomitant high rehabilitation costs. Third, utility functions are needed for Legacy program values, such as wildlife habitat and biodiversity. Utility functions for wildlife habitat will be developed based on general classes of wildlife and their responses to habitat factors. Biodiversity at the landscape level will be quantified using the methods of Loehle and Wein (1993). Other Legacy factors such as special habitats and archaeological sites, will be incorporated by giving a high weight to preservation of these fixed map locations during land-use allocation. Finally, it is necessary to incorporate optimization procedures into the SNRM system.

The entire SNRM methodology will be made compatible with military data systems via work performed at USACERL under this proposal. It will be designed to utilize Land Condition

Trend Analysis data, fit with ITAM and the goals of the Legacy program, and provide an integrated tool for the land-use considerations portion of the Carrying Capacity Model.

8. Expected Payoff:

The SNRM system will reduce costs, enhance land-use management responsiveness and effectiveness, disencumber military operations, enhance environmental compliance, and reduce conflicts between competing land uses. The system should also be usable at DOE and other federal facilities and for resource management on federal lands. In this way, dual-use technology will be developed with broad applicability to federal agencies.

9. Milestones:

(1) Develop generalized community landscape model, database of management options and costs, and utility functions based on training activity goals. Year 1.

(2) Integrate GIS, optimization, utility functions, diversity indices, and databases into a coherent software system. Year 2.

(3) Perform case studies and document system and results. Transfer technology to CERL. Year 3.

10. Transition Plan:

In order to transfer SNRM analytical tools to the military, ANL will arrange a technology transfer with USACERL. SNRM analytical tools are being designed to be compatible with USACERL systems, such as the GRASS GIS package.

11. Funding: ($K)

There has been no previous SERDP funding for this project. The proposed budget consists largely of personnel support, plus travel to visit military installations to acquire information. $100K/yr will be subcontracted to USACERL for their part in this work. This proposal is being simultaneously submitted via DOE and USACERL because it is a cooperative project. The proposed budget is as follows (in $1000s):

	FY94	FY95	FY96	Total
SERDP	433	433	433	1299

12. Performers:

Work will be performed by ANL and USACERL. Fort Riley, and at least one other military installation will be used as test sites.

ANL has extensive experience and expertise in environmental assessment, restoration, conservation, environmental compliance, GIS, and software development. Dr. Sundell has extensive experience in biogeographic research, land-use planning and natural resources management, spatial analysis, and environmental assessment, including the management of large projects funded by the U.S. Army. Dr. Loehle has published over 60 peer reviewed papers and

32 technical reports in ecological modeling, statistics, and environmental assessment and has developed sophisticated software systems. Ms. Sydelko administers the Land Resources Analysis Lab for the Energy Systems Division and has done assessment and applied research projects for the military, utilities, and DOE. Ms. Majerus is currently a Principal Investigator on the USACERL-ECS Spatial Analysis and Systems Team working within the Legacy Resource Management Program. She has administered research and development projects utilizing spatial, relational, and temporal data, spatial analysis and GIS (GRASS) technology, relational database management systems, and graphic user-interfaces for integrated natural and cultural resource management and ecological analyses for computer users on Army installations.

13. Principal Investigators:

Dr. Ronald Sundell, Dr. Craig Loehle, Ms. Pam Sydelko
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
TEL: (708) 252-5341
FAX: (708) 252-6407

Kim Majerus
U.S. Army Corps of Engineers
Construction Engineering Research Laboratories
Champaign, Illinois 61820
TEL: (217) 352-6511
FAX: (217) 373-7222

14. Keywords:

Conservation, Legacy, wildlife, habitats, Geographic Information Systems, ecological modeling

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Assessment and Management of Risks to Biodiversity and Habitat-2nd year renewal

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** ERL-Corvallis

5. **Proposal ID:** #241

6. **Problem Statement:**

Biodiversity, in the simplest terms, is the variety of life and its processes. Society recognizes a large variety of aesthetic, economic, conservation, and educational values associated with biodiversity. All of these are dependent on the following "first principles." Biodiversity is a manifestation of genetic diversity. It is the primary raw material that is filtered by natural selection, resulting in evolutionary and ecological adaptation of biota to environmental conditions. Minimizing additional loss of biodiversity will provide the best assurance that biota will adapt to the ever increasing rate and spatial extent of environmental change.

Traditionally, the management of biodiversity has focused on rescuing rare, threatened or endangered species from the brink of extinction. Huge sums have been spent on recovery programs for a small number of species. While there are strong conservation arguments for preserving these species, the effort expended has been out of proportion to the contribution that these species make to the genetic diversity, and therefore the fitness of the biota as whole to adapt to environmental stress.

The first year of this three year applied research project was funded in FY93. The current proposal requests funding for the second year of the project. It is part of a comprehensive interagency research effort to develop the technical information and data bases needed to assess and manage risks to biodiversity. The project specifically addresses Conservation Thrust Research and Development Objective #5, "Develop techniques to assess and predict the impact of military use of the areas on the critical elements of the ecosystem impacting biodiversity." Jointly, the Environmental Protection Agency, Department of Defense, US Fish and Wildlife Service, US Geological Survey, USDA Forest Service, and the Nature Conservancy will develop and test a risk-based paradigm for identifying those areas having species assemblages which contribute the greatest genetic diversity to the biota of their biogeographic regions and then managing those areas to sustain biodiversity.

Initially, this research will quantify relative risks to biodiversity in the west coast transect of states (Washington, Oregon, and California) and then evaluate the specific contribution of several high priority DoD installations to biodiversity along this transect. With SERDP funding, special emphasis will be placed on the contribution of DoD facilities to regional biodiversity in the pilot study areas. This research will be planned jointly with other SERDP funded research a DoD laboratories. In the future, we intend to develop a single, joint proposal to cover the biodiversity research now funded under this project and related SERDP funded research at DoD facilities.

7. Project Description:

This research will develop and test a new risk-based paradigm for identifying those areas having species assemblages which contribute the greatest genetic diversity to the biota of their biogeographic regions and then managing those areas to sustain biodiversity. The paradigm is implemented in two stages and at two greatly different spatial scales. First, priorities for management action are identified by comparative risk assessment across spatially extensive biogeographic regions. This permits cost-effective targeting of more intensive diagnostic and remediation efforts, allows accurate evaluation of the many species that have extensive geographic distributions, and avoids the pitfall of instituting protection at the local level, only to have cumulative effects of actions in the surrounding landscape undermine these efforts.

Secondly, specific remedial action plans are developed and implemented at a finer spatial scale (i.e., ecological subregions within a state) than the comparative risk assessment. At this scale, landscape level management approaches are needed. Attention will be directed to ameliorating the adverse effects of habitat fragmentation, reducing other forms of anthropogenic stress, restoring habitat, and evaluating the land management tradeoffs required to sustain biodiversity.

This research will initially categorize and map the species diversity and environmental diversity of sampling units (hexagons) based on the Environmental Monitoring and Assessment Program (EMAP) sampling grid covering the conterminous United States. The process will include (1) compilation of The Nature Conservancy's detailed vertebrate species distribution and attribute data for each hexagon, (2) compilation by hexagon of attributes of environmental diversity from remotely sensed land characterization data [AVHRR, TM or MSS based, depending upon results of pilot studies], and (3) analysis of the species and land characterization data by different ecological weighing methods, spatial analyses, multivariate statistical pattern analyses, and protection optimization methods. This information, along with stressor data compiled from existing databases [TIGER; USGS LUDA; USDA-NASS, ERS, NRI, FIA; USDI BLM] will be evaluated and synthesized to quantify relative risks to biodiversity. Overall patterns that lead to high importance and vulnerability of natural landscapes and biodiversity will be identified. Similar, but higher resolution methods will be used to characterize selected DoD installations. At this scale the emphasis is on the interaction between human activities and species habitat relations. Analyses will include spatially explicit evaluation of the causal mechanisms between landscape characteristics and ecosystem vulnerability to landuse practices. Data layers will include, if possible, 1) ecological characterization (terrain, soils, vegetation, rivers, streams, wetlands, lakes) 2) ecological inventory (species, ecological communities, Threatened and Endangered Species population data), and 3) Ecological Risk Characterization (Activity types, infrastructure, toxic releases, roads, anticipated future developments). These data will be used to develop scenarios of alternative futures for ecological systems, given alternative land management practices.

Methods need to be developed to bridge the hierarchy of space and time scales. Models and decision support systems are needed to allow effective transition between regional prioritization and resource allocation for biodiversity protection and local landuse management consistent with regional priorities. This project will evaluate theoretically based, practical approaches for handling these scale transitions.

8. Expected Payoff:

As managers of large areas of land, the DoD must fully evaluate its role in contributing to regional diversity. Benefits will include (1) establishment of baseline conditions concerning species distributions and their relationships with environmental diversity, (2) comparative risk assessment for biodiversity which identifies priorities for attention by the diversity of public and private land managers whose coordinated efforts will be necessary to sustain biodiversity and (3) testing of methods that hold promise for significantly reducing costs of habitat monitoring, evaluation, and management. Potential users will include virtually all land stewardship organizations concerned with the value of natural biotic resources.

9. Milestones:

Although the program's objectives are national in scope, several scientific issues will be addressed initially and resolved in an integrated series of pilot projects. These pilot studies will be completed over a three-year period (FY93-95). With SERDP funding, special emphasis will be placed on the contribution of DoD facilities to regional biodiversity in the pilot study areas. FY93 will be devoted to compilation of data bases and development of analytical methods. Data analysis will occur in FY94, with synthesis and final report preparation in FY95.

1.	Select and access first priority DoD installation	03/94
2.	Select and access second priority DoD installation	10/94
3.	Data for first selected installation	11/94
4.	Product: Spatially hierarchical planning framework	04/95
5.	Data bases for West Coast Transect (Species occurrences, AVHRR derived Landscape data, Landscape stresses - by EMAP hexagon for Washington, Oregon, and California)	06/95
6.	Product: Alternate futures (First Installation)	08/95
7.	Data bases for second selected installation	10/95
8.	Product: Alternative futures (Second Installation)	04/96
9.	Product: Biodiversity Conservation Priorities (West Coastal States Demonstration)	04/96
10.	Product: Multiscale Biodiversity Planning & Management	10/96
11.	Product: Final Report	01/97
12.	Workshops at DoD installations (Tech Transfer)	02/97

10. Transition Plan:

This three year effort is a portion of an integrated series of pilot studies designed to develop and evaluate methods for a national assessment to be conducted in 1997 and 1998. On completion of the national assessment, it will be possible to objectively assign priorities for biodiversity protection nationwide.

11. Funding: ($K)

	FY93	FY94	FY95
SERDP	1000	1325	1000
EPA	500	500	500
TOTAL	1500	1825	1500

12. Performers:

In recognition that loss of biological diversity can only be effectively addressed through cooperation of vested interests, EPA has formed a biodiversity research consortium to develop the technical information and data bases needed to assess and manage risks to biodiversity. Membership in the consortium includes the US Fish and Wildlife Service, USDA Forest Service, USDI Geological Survey, and The Nature Conservancy, and the Department of Defense. Additional participants are funded through cooperative research agreements, including: University of California - Santa Barbara, University of Maine, Oregon State University, and Harvard University. The Department of Energy, Oak Ridge National Laboratory participates through Interagency Agreement. The project will be coordinated with DoD's Legacy Biodiversity Task Area, as it develops, to maximize complementarity and avoid redundancy. We propose that the Biodiversity Research Consortium focus on database acquisition and analysis and the DoD have the lead role in developing specific recommendations for biodiversity on the installations studied.

13. Principal Investigator:

Dr. Eric M. Preston
U.S. EPA Environmental Research Laboratory
200 SW 35th Street
Corvallis, Oregon 97333
TEL: (503) 754-4459
FAX: (503) 754-4338

14. Keywords:

Biodiversity, conservation, EMAP, ecosystem stress, endangered species, habitat, landscape management, DoD lands, land stewardship

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Conservation

2. Title: Threatened, Endangered, and Sensitive Resources

3. Agency: Army

4. Laboratory: CERL

5. Proposal ID: #507

6. Problem Statement:

Goal: Our goal is to establish the Army and participating services as national leaders in proactive conservation of threatened and endangered species (TES) and the ecosystems upon which they depend as an integral part of our mission. This research will contribute to an overall programmatic effort to provide capabilities to avoid mission impacts while enhancing efforts to meet national, DoD, and Army TES-related conservation goals cost-effectively. It addresses subelements of the Army's highest Conservation Pillar R&D requirement, "Impact of Military Operations on TES."

Problem Statement: More than 800 species are protected under the Endangered Species Act (ESA); while thousands more are candidates for listing. Many reside on military lands, resulting in: (1) mission constraints and impediments to land acquisition, potentially leading to reduced defense readiness; (2)lengthy and costly litigation; and (3) criminal and civil penalties. As the number of listed species increases, mission constraints and management burden also increase. Our ability to address this issue is limited because of inadequate information on the effects of mission activities on TES and supporting ecosystems.

R&D Objectives: The major objectives of the proposed research are to develop and evaluate protocols to generate threshold models of the impacts of smokes, obscurants, and CS agents on TES, and to initiate research leading to threshold models for habitat disturbance. The requirements addressed here are critical subelements of the Army's highest Conservation Pillar R&D requirement (i.e., Impacts of Military Actvities on TES) as determined at a recent Army Conservation Pillar user requirements prioritization workshop. (A third subelement of this requirement focuses on noise impacts. This latter topic is addressed under a separate proposal in the Compliance Pillar.)

Project Status/Research Category: This is a new applied research project.

7. Project Description:

Technical Objective: Our objective is to continue research inititiated under previous SERDP funding to determine the impacts of military-related chemicals on TES, but narrowed to focus exclusively on smokes, obscurants, and CS agents. This work will also initiate studies to develop threshold models of impact on TES due to maneuver and related habitat disturbance.

Technical Approach: There is a clear need to evaluate the impact of mission activities on TES to meet ESA's biological assessment requirements, and as a basis for defining appropriate levels of TES protection. Direct impacts due to training/testing activities on species as well as indirect impacts due to habitat degradation and fragmentation must ultimately be addressed. Practical approaches and techniques will be developed that can be applied at the installations level.

Smokes, Obscurants & CS Agents: A thorough evaluation of existing documentation on the use of S-O&CS; the known and probable impacts of these materials on plants and animals, including an evaluation of materials currently in development; and research protocols currently applied will be completed. Smoke toxicity thresholds will be determined based on existing documentation and selected laboratory studies. We will determine which species are most likely in jeopardy due to exposure to these materials, and which mission activities are most likely constrained significantly as a result of species sensitivities. Up to two species will be selected for study on one or more installations based on a risk assessment evaluation. A conceptual approach to development of threshold models for the impacts of S-O&CS on TES will be developed. Field research protocols developed shall serve as the basis for preliminary field studies on selected species to be conducted under this work. Complete field evaluations beyond preliminary studies are contingent upon follow-on funding.

Habitat Disturbance: Military activities can adversely affect TES by degrading habitats upon which these species depend. These impacts can be either instantaneous resulting in immediate site abandonment or mortality as well as cumulative over time, resulting in a slow degradation of TES carrying capacity and species vigor. Species will differ in their response and resilience to such impacts. The first step in evaluating thresholds of response to habitat disturbance will be to identify an exhaustive list military activities that may affect TES habitats, followed by an evaluation of the probability that these resulting disturbances will affect species of interest. This assessment will be based on types of military activities in practice and how they are conducted during realistic training and testing scenarios. Species will be selected for follow-on studies based on this analysis. A conceptual approach to development of threshold models applicable to habitat disturbance impacts on TES will be developed.

Relationship to DoD/DOE Environmental Objectives: The proposed work supports many of the Departments' goals and objectives as specified in SERDP guidance documents. Specifically, our intent is to: (1) provide capabilities to unencumber military operations while protecting sensitive resources cost-effectively, (2) contribute leadership in addressing a pressing national environmental problem, (3) facilitate information exchange among governmental and nongovernmental agencies and the private sector, (4) avoid duplication of effort among these groups, (5) investigate potential applications of technologies developed for national defense purposes, and (6) encourage joint interagency R&D and demonstration projects.

Relationship to Similar On-going Work: Related FY93-funded SERDP projects include:"Regional Approaches for Managing TES Habitats on DoD Lands," "Propagation, Translocation, and Reestablishment of TES," and "Identification, Assessment, and Mitigation of Impacts of Military-Related Chemicals and Pollutants on TES." On-going research under the Army's Long Range Science and Technology Program (LRS&T) includes: "Proactive Mitigation and Management of TES on Army Lands," "TES Enhancements to the U.S. Army LCTA Systems Development," and "Inventory and Monitoring Standards for TES on Army Lands." Several additional TES and related projects are funded under DoD's Legacy Resources Management Program. Close coordination will take place with each of the organizations, activities, and projects identified above in order to avoid duplication of effort.

Tri-Service Environmental R&D Strategic Plan: This work is intricately related to DoD Pillar #4, Conservation. The specific thrusts directly addressed is 4.P: Training/Testing Impact Analysis on T/E.

8. Expected Payoff:

These efforts will contribute one piece to a comprehensive, systematic, and integrated approach to TES management on military lands. Resulting products will support the Army's environmental and endangered species management strategies, and aide in efficiently meeting Army TES policies and regulatory requirements. Through this effort, the military will develop and demonstrate scientific and technical leadership in the management of TES. We will thus be better able to integrate TES considerations with military activities while avoiding mission impacts. Expected return on investment is high. On-going interagency coordination will yield benefits at national, regional, and local levels. Potential users include Army and other military elements at installation, MACOM, and DA levels who are responsible for TES management. Products will also transition to interagency and private sector partners.

9. Milestones:

Smokes, Obscurants, & CS

1.	Evaluate existing documentation regarding impacts of smokes, obscurants & CS (S-O&CS) on TES	6/94
2.	Develop list of species most likely to be impacted by S-O&CS; evaluate probable impacts	8/94
3.	Select species and sites for field studies	10/94
4.	Conceptual approach for threshold models addressing S-O&CS	3/95
5.	Determine smoke toxicity levels for selected species	6/95
6.	Initiate field evaluations of protocols in preliminary field studies	6/95
7.	Complete field work	6/96
8.	Report results of field work; recommendations for follow-on studies	9/96

Habitat Disturbance

1.	Develop extensive list of training activities with known or probable impacts on TES habitats	9/94
2.	Evaluate probable impacts on TES habitats due to specific military activities	12/94
3.	Conceptual approach for threshold models addressing habitat disturbance	6/95
4.	Report research results; recommendations for follow-on studies	9/95

10. Transition Plan:

Technology transfer is an essential element of the proposed work. We are committed to developing useful technology from research projects while reaching out to a broad range of potential users. This includes relevant technologies developed by other TES programs, and distribution of transfer products to government, nongovernment, and private sector entities. A TES Technology Transfer Plan will be prepared and coordinated with related military land management programs under separate funding. Coordination will occur via a high degree of

interaction with the user community through user group workshops, periodic newsletters and information bulletins, and eventual use of alpha- and beta-test sites for technology demonstrations.

Several federal agencies presently conduct TES-related research; much of it applicable across agency lines. Mechanisms will be established to share information, and to coordinate TES R&D with appropriate government and nongovernment agencies and other public and private sector organizations. We will avoid duplication of effort, identify opportunities to leverage limited resources to meet common goals, and maximize transfer and use of the best and most advanced technological capabilities available.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
S-O&CS	500	558	349	000	1407
Habitat Disturbance	305	000	000	305	
TOTAL	805	558	349	000	1712

12. Performers:

The work will be conducted primarily by USACERL with assistance from other COE Labs and Army research elements, with an emphasis on leveraging opportunities. Relevant capabilities exist at Waterways Experiment Station, Cold Regions Research and Engineering Lab, Topographic Engineering Center, and Edgewood Research, Development and Engineering Center. Leveraging opportunities will be also be sought with government and nongovernment agencies and the private sector via interagency cooperation efforts.

13. Principal Investigator:

Dr. Dave Tazik
Natural Resources Division
USACERL, PO Box 9005
Champaign, IL, 61826-9005
TEL: (217) 373-4420 x 606
FAX: (217) 373-5420

14. Keywords:

Threatened and Endangered Species, Military Impacts, Smokes, Obscurants, CS Agents, Habitat Disturbance

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Integration of Radiotelemetry, Remote Sensing and GIS Technologies for Habitat Use and Delineation in Support of Risk Assessment and Restoration Activities.

3. **Agency:** WSRC/DOE

4. **Laboratory:** Savannah River Technology Center (SRTC)

5. **Proposal ID:** #363

6. **Problem Statement:**

The goal of the proposed program is to integrate automated radiotelemetry with Global Positioning System (GPS), Geographic Information System (GIS), and over flight land cover information in a way that will increase efficiency, accuracy, and availability of habitat and land cover use data necessary for a variety of ecological activities including:

- waste site characterization
- ecological risk assessment
- performance and success of ecosystem restorations
- habitat use of animal species of concern, such as those listed as threatened or endangered

Historically, habitat use and preference has been very difficult to quantify for many types of organisms. For larger animals, these data are generally collected using radiotelemetry, a method where small radio transmitters are attached to the organisms to be studied. The animals are then located using hand-held antennas connected to portable receivers. Locations of the animals are then surveyed or approximated on a map, or the habitat and cover type are simply recorded. This method requires extensive field time and provides very limited data return for time invested. Organisms available for study are also limited to those large enough to carry radio transmitters, data for small animals can only be collected through extensive field observation. Current technology in miniaturization is lending itself to much smaller radio transmitters, allowing them to be attached to smaller organisms (i.e. bats, small rodents, snakes, and frogs). There is however still the problem of data density, or the amount of information obtained per unit of effort. Automated telemetry systems coupled with existing information technologies could greatly enhance the usefulness of radiotelemetry for habitat use data collection.

7. **Project Description:**

Technical Objective:

- Refine the existing automated telemetry system with hardware and software upgrades
- Develop software to use data from the automated telemetry system to calculate locations from triangulation
- Interface triangulation locations with GIS layers of habitat types developed from other remote sensing techniques like GPS and over flight data.
- Field test of upgraded equipment within a potential risk assessment area at SRS

Technical Approach: The principle technical approach is to integrate existing hardware previously developed by SRTC with other available remote sensing and information management systems. This will be accomplished through further development of the existing hardware and its control software and development of interfaces to other technologies. Full scale field research will provide testing and verification of the technical approach.

Tasks:

- Field test of the existing equipment
- Upgrade of existing hardware to increase capabilities and speed
- Development of triangulation/data analysis software
- Development of GIS interface
- Field test of data acquisition portion of project
- Test of integration algorithms and data analysis
- Publication of results

Relationship to DoD/DOE environmental objectives: This program supports the mission and objective of DoD/DOE to be leaders among government agencies in applying modern technology to ecological risk assessment, restoration, remediation, and the preservation and enhancement of biological diversity. Specifically, this program endeavors to apply new approaches to old problems of determining specific habitat preferences and use by animals within limited areas. By better elucidating how organisms interact with their habitat on a small scale, ecologists will be much better able to determine what risks a waste site may pose to the surrounding ecosystem.

Relationship to other similar ongoing work: The proposed project is a considerable expansion of a program initiated during research supporting proposed actions for continued operation of L and P Reactors at SRS. Lotek Engineering, Inc. was commissioned to design and build an automated radiotelemetry tracking system centered around their very advanced SRX400 receiver. The system is capable of monitoring up to 400 different radio frequencies and can provide automatic relocation of transmitters as often as every five minutes. The system was intended to monitor movements of fish in response to elevating temperatures during start-up of L and P Reactors. This data was to be an important basis for strategies to minimize fish kills during reactor start-up. Unfortunately, the decision to not restart L or P Reactor obviated the need for the system. Upgrading the existing system and integrating it with other remote sensing and information management technologies will allow more accurate and scientifically defensible characterization and evaluation of waste sites for ecological risk assessment.

8. Expected Payoff:

Benefits accrued from the development of automated radiotelemetry and its interface with other remote sensing technologies and GIS could be enormous. The development of very powerful desk top computer data management systems (HOPPS for example) will simplify sophisticated analysis of habitat use data. Data collected and analyzed with the proposed system is useful and necessary for many compliance related activities like Natural Resource Damage Assessment (NRDA) activities, characterization of waste sites prior to ecological risk assessment, actual effects and vectors in indicator organisms chosen for ecological risk assessment, and recovery of populations and habitat use within restored ecosystems. The capability of the proposed radiotelemetry system will supply data density on habitat use an order of magnitude greater than possible with current systems. This will reduce cost of acquiring necessary information and will provide the benefit of allowing collection of data that is not currently possible to

accumulate. Parameters like patterns of habitat use, home range, and behavioral use of space are currently difficult to determine but are important considerations in the evaluation of ecological risk. The ability to precisely evaluate these parameters will greatly improve the accuracy of ecological risk assessment activities.

9. Milestones:

1.	Field test of original automated telemetry system	3/94
2.	Plan hardware upgrades	5/94
3.	Begin development of data handling software	7/94
4.	Begin development of GIS interface software	8/94
5.	Begin to implement hardware upgrades	10/94
6.	Complete all upgrade and software development	6/95
7.	Begin field test of upgraded equipment	8/95
8.	Use field test data for GIS interface demonstration	6/96
9.	Publish results	12/96

10. Transition Plan:

Capabilities of the system will be will be documented and publicized through publication of the results of the field test of the upgraded system and the analysis of the data collected. Transition of the telemetry system itself will be handled by Lotek Engineering, Inc. through their established private sector marketing network. Transition of the data analysis and GIS interface software will be accomplished cooperatively by the contributors to the program with the assistance of the Technology Transfer organization within WSRC.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	0	200	200	600
DOE/WSRC	25	25	25	75
TOTAL	225	225	225	675

Previous funding: Expenditure by SRTC/ESS for development of the original automated equipment, approximately $125,000.

12. Performers:

Currently the only performers involved in the project are SRTC and Lotek Engineering, Inc. There have, however, been contacts from researchers at Pacific Northwest Laboratory (PNL) and The Institute for Wildlife and Environmental Toxicology (TIWET) at Clemson University regarding the development of the data analysis and GIS interface aspects of the proposed project. Time constraints have precluded any detailed agreements or firm commitments from these organizations, but they will be pursued and defined in the next few months.

13. Principal Investigator:

Lynn D. Wike, Ph.D.
Senior Scientist A, Ecology Group
Building 773-42A
Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, South Carolina 29802
TEL: 803-725-5210
FAX: 803-725-7673

14. Keywords:

Radiotelemetry, Remote Sensing, Ecological Risk Assessment, Habitat Use, Geographic Information Systems, Global Positioning System

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Fishing Enforcement/Whale Monitoring Using IUSS

3. Agency: Navy

4. **Laboratory:** Space and Naval Warfare Systems Command

5. **Proposal ID:** #048

6. Problem Statement:

The goal of this effort is to continue to apply capabilities of the U.S. Navy Integrated Undersea Surveillance System (IUSS) to support the High Seas Driftnet Fisheries Act (PL102-582) and other national treaty and maritime law enforcement requirements, and to monitor various species of marine mammals to contribute towards conservation and regulations compliance. This work explicitly supports the SERDP Goal to "help solve significant...environmental problems through the application of (DoD's) technical capabilities...", several SERDP Objectives, all four SERDP Strategy Statements, and Conservation Pillar R&D Objectives 1,3, and 5.

The IUSS provides a unique resource to monitor the population and movements of several endangered marine mammals -- specifically, the great whales. In no other way can these movements be monitored over the scale of an ocean basin. Exploitation of this resource is vital in complying with the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA), and the Marine Mammals Protection Act (MMPA).

Present utilization of the IUSS to detect and classify marine mammals (and drift net vessels) is a personnel-intensive effort. Projected downsizing will reduce the operational personnel currently monitoring IUSS fixed arrays on a 24-hour basis. One important component of this effort will be to automate the detection and classification processes using neural network signal processing techniques.

When this project was presented to the SAB in April, the Chairman commented that this "was precisely the kind of project Senator Nunn had in mind when he created SERDP." Other panel members were uniformly supportive of the effort.

7. Project Description:

This project will build on the substantial success of the past year and will further enhance the methodologies to exploit the IUSS in support of a variety of national objectives.

The Navy demonstration project "WHALES '93" paved the way for the first objective, quantitative analysis of whale populations and migratory movements. Other agencies, particularly NOAA, have become convinced of the need to further the results of that effort in order to refine these capabilities into operational tools. The objectives and work of this proposal have been coordinated with SERDP proposals submitted by NOAA and is complimentary to that proposed work.

In the next year, this project will focus on three main fronts: (1) a major experimental effort on whales in the Pacific Ocean; (2) accelerating the development of neural net processors; and (3) enhancing the interface between the IUSS and potential users.

On the first objective, the goal is to identify the migratory path(s) of humpback whales (Megaptera novaeangliae) in the northeastern Pacific Ocean. The whales are generally known to migrate between feeding grounds along the Pacific coast of North America (SE Alaska to northern California) to breeding grounds off Mexico and Hawaii. (The Hawaiian breeding grounds will be the focus of this effort.) Humpback whales migrate south to the breeding grounds during the fall (Sep-Dec) and return north in the spring (Mar-Jun). During the first round-trip migration, the project will focus on perfecting capabilities using only a few of the fixed arrays. During the second migration, the effort will focus on perfecting the techniques for localization and tracking, and to concentrate on areas of special interest revealed during the first migration. This experiment will be carried out by NRaD Code 51 and will make primary use of the fixed arrays, but will also request the use of mobile IUSS assets (i.e., SURTASS) on a not-to-interfere basis. At both ends of the migratory path there are well-established programs of study (University of West Oahu, Dr. J. Mobely, PI; NOAA National Marine Mammal Laboratory, Dr. M. Dahlheim, PI). These will enable us to link IUSS data to the types of data that have traditionally been gathered by shore-based programs of study.

On the second objective, work on neural network signal processing technology will be enhanced by other work on an improved IUSS beamformer that would give constant beamwidth coverage over the bandwidth of interest, and an improved coherent interarray processing (IAP) capability that will allow more precise localization of specific activities of interest. All of these individual capabilities have been partially developed in a somewhat different form for military applications. The neural network processing capability already exists in a form that could be readily adapted to the marine mammal problem. The design of an improved constant-mainlobe adaptive beamformer has essentially been designed under another effort and is more than 50% complete. The coherent interarray processor (IAP) requires software upgrades that would allow it to work more effectively against the broadband transient signal types which represent most whale vocalizations. The target site for the proposed demonstration will be the Naval Facility (NAVFAC) at Whidbey Island, WA.

For the final objective, full use will be made of the Dual Use Analysis Center (DUAC) which has been built at the Naval Research Laboratory. The DUAC, a secure facility, was created to establish a link between the researcher and the day-to-day operations of the IUSS, with initial emphasis on data acquired during the WHALES '93 Experiment. Initially, significant hardware needs of the DUAC will be met so that the enormous data sets of WHALES '93 can be effectively archived and processed. Then, a system-wide data archiving capability will be developed; i.e., a system that "records everything", as requested by the Environmental Task Force. In the final years of this project, prototype communications links will be established at the DUAC so that users can access IUSS information in an unclassified setting.

This proposal addresses several requirements identified in the Tri-Service Environmental Quality R&D Strategic Plan under Conservation Thrusts 4P (Training/Testing Impact Analysis on T/E) and 4Q ((T/E Species Management, Propagation, and Recovery).

8. Expected Payoff:

The benefits of this project come in two main areas. The first if through gains in our understanding of an endangered species with a large range. If the humpback whale's movements and the timing of the movements are known more precisely, the Navy and other users of the range shared with the humpback can plan their activities to minimize the impact on the whales. The development of the automated methods for whale tracking will be of particular value to NOAA and other agencies tasked with protection and management of endangered species. Second, this project will enable the opening up of an ocean-wide network of sensors that is otherwise unattainable by the research community. A primary deliverable of this effort is a user-friendly "portal" to Navy's undersea surveillance system. In a time where "big science" costs are being closely scrutinized, it is particularly attractive to consider access to a system which is already paid for.

9. Milestones:

From FY93 funded program:

1.	Final Report, WHALES '93	06/94
2.	Final Report, North Pacific Driftnet Experiment	09/94

For FY94 and following years program:

1.	Complete design for auto-demo system for single site	10/94
2.	Coordinate activities of PAC/Whales Experiment	01/95
3.	Complete hardware/software for initial auto-demo	02/95
4.	Run simulation of PAC/Whales, set up equipment	03/95
5.	Data collection on first PAC/Whales northward migration	06/95
6.	Analysis of initial PAC/Whales migration	09/95
7.	Initialize collection on first southward PAC/Whales	01/96
8.	Complete modification of IAP	02/96
9.	Complete demo of user-friendly access at DUAC	03/96
10.	Complete integration of components for auto-demo system	06/96
11.	Data collection, second PAC/Whales migration	06/96
12.	Final report, PAC/Whales	09/96
13.	Demonstrate automated detect, classify, track capabilities	06/97
14.	Installation of comprehensive archiving capability	09/97

10. Transition Plan:

A close working relationship has been established with NOAA, which would be the primary beneficiary of many of the results gained here. A Memorandum of Agreement has been signed by NOAA and Navy on cooperation on environmental issues, and will serve as the umbrella MOA for further agreements which arise from cooperation in this area. In addition to the benefits highlighted with marine mammals (supporting NEPA, ESA and MMPA), the IUSS network will provide the means to monitor fishing activity (in support of national programs and international treaties), mid-ocean seismic and volcanic activity and acoustic tomography studies (in support of global warming studies).

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	3000	3000	2500	2500	2500	16500

12. Performers:

A. Humpback Migration Task: Naval Research and Development Center (NRaD), Commander, Undersea Surveillance Pacific (CUSP), Lawrence Livermore National Laboratory, NOAA Southwest Fisheries Center, NOAA Marine Mammal Laboratory, NOAA Pacific Marine Environmental Laboratory, University of West Oahu, Woods Hole Oceanographic Institution.

B. Signal Processing Task: Naval Research and Development Center (NRaD), ORINCON Corp., ENSCO Inc.

C. IUSS Interface Task: Naval Research Laboratory, MITRE, MAI, Cornell University.

13. Principal Investigators:

Dr. Dennis M. Conlon, Chief Oceanographer
Integrated Undersea Surveillance Program (PMW182-OC)
Space and Naval Warfare Systems Command
2451 Crystal Drive
Arlington, VA 22245-5200
Tel: (703) 602-1021
Fax: (703) 602-0123

The task on humpback whale migration will be managed by:

Dr. Robert Gisiner
NCCOSC RDT&E Division, Code 511
49650 Aoucstic Rd, Bldg. 112
San Diego, CA 92152-6250
Tel: (619) 553-5592
Fax: (619) 553-5691

14. Keywords:

IUSS, Acoustics, Whales, Neural Networks, Fisheries, Migration

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Conservation

2. Title: The Effects of Aircraft Overflights on Birds of Prey

3. Agency: United States Air Force

4. Laboratory: Armstrong Laboratory

5. Proposal ID: #089

6. Problem Statement:

The goal of this project is to verify predictions of a previous 6.3A effort regarding the effects of aircraft noise on birds of prey or raptors (hawks, eagles, falcons, etc.) and to fill in the technological gaps in the interim model.

The Air Force is required to assess the impact of proposed aircraft operations on the environment. Many of the assessments accomplished to date contain unsubstantiated remarks concerning the effects of aircraft noise on wildlife. Prior to 1989 noise studies on wildlife were not well controlled or planned. In 1989 the Air Force began performing several 3-4 year studies on the effects of aircraft noise on wildlife species. These studies are beginning to prove useful for environmental planners at the major command and Air Staff level to defend the Air Force's requirements to maintain low altitude Military Training Routes (MTR).

Due to issues raised during public scoping meetings and documented concerns with the US Fish and Wildlife Service (USFWS) and the National Park Service (NPS) there is concern that aircraft overflights may disturb nesting raptors. The Air Force embarked on a project in 1989 to review the current literature regarding the effects and, if feasible, develop an interim model to predict the effects. The interim model was documented in 1990. Since the model is purely hypothetical, it must be validated with empirical data.

7. Project Description:

The technical objective of this project is to develop a validated dose-response model on the effects of aircraft overflights on birds of prey. The technical approach to accomplish the objective will be to perform field studies on species of interest in an attempt to validate the current model.

Several tasks will accomplish this objective. Task 1, a study protocol will be developed in cooperation with the USFWS to perform valid field studies to detect differences of 5-30% productivity rates in spite of large variances in nest success. The study design will take into account such factors as habituation rates, prey abundance, and changes in parental behavior that could affect productivity. This first task will examine possible study locations and make a recommendation for the best sites near an Air Force installation to perform such a study.

Task 2 will be designed to make observations of aircraft overflights in the vicinity of nesting raptors. This task should be performed over a two year period as a minimum to determine the effects of noise on productivity.

Task 3 would attempt to address the effects of aircraft overflight noise on threatened or endangered raptor species, such as Peregrine Falcons and Bald Eagles. This task would form a subset of data obtained from Task 2 where nonthreatened and nonendangered species would be studied.

Task 4 will involve making changes to the current dose-response model and inserting the improved model into the latest version of the Assessment System for Aircraft Noise (ASAN). ASAN is a software tool to assist environmental planners assess the impact of aircraft operations on the environment.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 4: Conservation; Requirement Thrust 4.K: Sensitive Ecosystem Management and 4.P: Training/Testing Impact Analysis on T/E.

8. Expected Payoff:

The Air Force will benefit by having a validated model to assess the impact of aircraft noise on raptors. This will greatly assist environmental planners in developing timely EIAP documents and providing answers to questions raised by the general public, USFWS and NPS. Currently, the USFWS can and has stopped proposed actions with formal Section 7 consultations in accordance with the Endangered Species Act. The goal of this project would be to reduce the concerns raised during these formal consultations and speed up the EIAP.

9. Milestones:

1.	Research protocol and recommended study sites.	9/94
2.	Experimental data on nonthreatened/nonendangered species.	9/96
3.	Experimental data on threatened/endangered species	9/97
4.	Dose-response model inserted into ASAN	9/97

10. Transition Plan:

The dose-response model resulting from this effort would replace the current interim model in ASAN. ASAN is scheduled to begin transition in FY94. Since ASAN will accept various effects modules, there will be no risk in changing these two models.

It will be necessary to coordinate aircraft overflights with the nearest operating command to the study site. Since several previous studies similar to this proposal have been accomplished, these procedures are well known.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	80	311	518	285	1194

12. Performers:

The Air Force Armstrong Laboratory will be the principal agency performing this work with support from the Air Force: AL/OEBN and 11th AF/DOO and 11th AF/LGV. Additionally, the Alaska Fish and Wildlife Cooperative Unit and the University of Alaska along with Alaska Biological Research, Inc. will also participate in this research.

13. Principal Investigator:

Major Robert C. Kull, Jr.
AL/OEBN
Wright-Patterson AFB, OH 45433-7901
TEL: 513-255-3605
FAX: 513-476-7680

14. Keywords:

Raptors, Birds of Prey, aircraft noise, disturbance

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (Systemic, genetic, immune and reproductive toxicity evaluation of munitions-impacted terrestrial and aquatic fauna)

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** Environmental Monitoring Systems Laboratory, Cincinnati, Ohio

5. **Proposal ID:** #244

6. **Problem Statement:**

Goal: 1) To apply biomarkers (physiological, biochemical and molecular changes in wild fauna), as tools to assess and monitor impacts of defense-associated chemical production and applications, (e.g. munitions manufacturing, open detonation and open burning, decommissioning and de-arming chemical agents, fuel refining and storage, machine de-greasing wastes, and chemical by-products) on sensitive aquatic and terrestrial fauna at selected DoD facilities; and 2) to establish patterns of biomarker changes, via comparative studies of native fauna in contaminated and reference sites, that are useful for demonstrating the probability of ecosystem-level impacts from these materials.

Background: The DoD has concerns about the potential ecological consequences associated with soil and water contamination by explosives, and the intermediates and by-products of explosives resulting from the synthesis and degradation of these materials. Munitions products, e.g., hexahydro-1,3,5,-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro,1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT) and by-products (e.g., dinitrotoluenes, trinitrobenzene and dinitrobenzene)are frequent contaminants at DoD facilities. They are degraded by microorganisms under anaerobic conditions to numerous by-products, however, the short and long term effects of exposure to these materials on ecological resources are unknown and data establishing the impacts (or indicating absence of impact) are generally not available. For this reason, DoD is often unable to conduct scientifically defensible, risk-based assessments of the potential impacts imparted by this class of ubiquitous chemicals to feral species and native plants in the vicinity of the affected installations.

This project will assist DoD in developing a quantitative data base for ecological assessments. This proposal will develop biochemical markers of exposure and effect on widely distributed and ecologically important species. These biomarker data will be evaluated, and the changes will be correlated with existing ecological resources in impacted and reference sites. The results will be used in a diagnostic mode to assess the impacts of the munitions contaminants, to prove or disprove the cause-effect relationships, and to guide clean up and restoration activities. In conformity to processes presented in the EPA's *Framework for Ecological Risk Assessment*, the project effort will emphasizes the definition of assessment and measurement endpoints and their interrelationships and the characterization of risk across various levels of ecological organization.

7. Project Description:

Previous Efforts/Accomplishments: The scientific staff at the Ecological Monitoring Research Division (EMRD), Environmental Monitoring Systems Laboratory (EMSL), U.S. EPA have extensive training, hands on experience and expertise in the areas of research that are required to carry out the proposed project successfully. They have a continuous record of peer reviewed publication in research on biomarkers. Currently, EMRD has an interagency agreement with U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, MD to conduct studies on the adduction of nitroaromatic compounds with blood proteins and DNA as biomarkers of exposure. Likewise, EMRD has developed and field tested sets of biomarkers in feral fish for the assessment of exposure and effects of industrial contaminants.

Experimental Overview: This project will: 1) apply and validate, using previously established technology and expertise, an integrated matrix of biomarker endpoints for assessing exposure and effects of munitions-related contamination under laboratory and field settings, and 2) evaluate the utility of this biomarker matrix as a tool to provide DoD with advanced assessments of munitions-related contamination at various ecosystem levels.

Technical Approach: 1) Site selection will be focused on those munitions-contaminated installation(s) which are located at a strategic proximity to ecologically appropriate reference site(s). 2) The contaminated and reference sites will be inventoried and lists of ecological assets will be compiled. Suitable measurement endpoints will be selected on the basis of the biomarker methods available and on the ecological resources to be monitored. 3) The biomarker profiles of selected wildlife will be compared in the contaminated and impacted sites and referenced against the status of the ecological assets. 4) Biomarkers that appear useful as predictive of ecosystem impacts will be identified for future assessments at other DoD facilities.

Laboratory studies necessary to support the verification of field results will accompany the field studies. Examples of specific endpoints which can currently be utilized in these biomarker studies include:

- Biochemical Toxicology (e.g., quantitation of DNA and blood protein adducts, bile metabolites,and speciation of altered heme synthesis intermediates (porphyrins) as biomarkers of exposure to selected chemical classes; application of cDNA probes for detection of gene expression (e.g., cytochrome P450Ia1), utilization of hepatic microsomal enzyme activities indicative of xenobiotic induction. (EROD, AHH, Glutathione)
- Molecular Histopathology (e.g., optical and electron micrography, in combination with computer-assisted image analysis and immunobased, pathology specific histochemistry.
- Molecular Biology (e.g., the detection of genotype distributions within a population and losses of genetic diversity via polymerase chain reaction technology for DNA finger printing and electrophoretic allozyme frequency analysis.
- Cellular and Organ Immunotoxicology (e.g., quantitative measure of phagocytosis and immune suppression, characterization and quantitation of oxidative burst capacity in phagocytic cells via laser activated fluorescence flow cytometry and cell sorting.
- Reproductive Toxicology (e.g., computer assisted sperm motion analysis and flow cytometric characterization of spermatogenesis, sex hormone patterns, gonadal pathology, and developmental anomalies.

Unique Assets Offered: The Ecological Monitoring Research Division (EMRD) of the U.S. Environmental Protection Agency offers the following assets and capabilities: 1) A highly

qualified research staff including 14 Ph.D. level scientists (degrees in ecology, toxicology, biochemistry and molecular biology) with substantial records of peer-reviewed publication. 2) State-of-art laboratory instrumentation as well as significant and proven experience in field sampling, sample preservation, transport and logistics. 3) A modern, accredited animal research facility uniquely equipped and a staff experienced in handling animal husbandry for a variety of terrestrial and aquatic species. (The Division has developed breeding colonies of terrestrial (field mice, voles, and shrews, invertebrates, and plants), and aquatic (fish, tadpoles, invertebrates and plants) organisms. 4) A fully staffed aquatic research facility with a wide range of aquatic ecotoxicological and bioassessment capabilities.

Innovative Elements: This research is innovative in that traditionally, biologically derived information about ecological impacts have been limited to traditional evaluations of community structure and the direct measurement of tissue residues. Biological markers provide predictive and diagnostic information not only to detect exposure, but also to detect early effects of these exposures, and to identify causes. Biomarkers can focus efforts where they are most needed for the protection of wildlife; e.g., on contaminants that are biologically available, which bioaccumulate, and which are biologically active (e.g., toxic).

Relationship to DoD Environmental Objectives: This project will directly support the Conservation Strategy by providing quantitative indicators of the health status of the impacted fauna, leading to enhanced ecological risk assessment. The DoD is in the process of establishing the toxicological and ecological data base for determining the potential environmental effects of munitions chemicals that have been discharged in the environment over years. Technical Issues to Overcome: 1) The selection of appropriate site(s), and coordination with other research organizations dealing with the site studied, 2) the selection, from appropriate existing or new biomarkers, those most appropriate for detection and assessment of exposure to munitions compounds, and 3) development of systematic methods for using biomarker data to assess and predict ecosystem impacts.

8. Expected Payoff:

The proposed project will incur five major benefits to DoD: 1) It will provide a quantitative means to prove or disprove cause-effect relationships between munitions byproducts contamination and ecological effects. 2) It will provide baseline data to assess the ecological impact of munitions activities, thus, it will assist in planning remedial intervention. 3) In terms of impact, (cost/time/efficiency/capability) it will provide means of documenting the cost effectiveness of ecological interventions. 4) It offers the possibility of significant improvements in the timeliness of the ecological assessment process. 5) It will assist in evaluating/ reestablishing genetic and biodiversity particularly of sensitive and endangered species at impacted area.

9. Milestones:

1993-94: In collaboration with DoD: Conduct site(s) selection(s) [including appropriate reference site(s)], develop and finalize biomarker matrices (both for aquatic and terrestrial systems) determine appropriate research protocols and quality assurance issues, prepare plans for awarding cooperative and interagency agreements and/or grants to perspective DoD and other US Government collaborators.

Initiate Collaborative Instruments (e.g., IAG)	12/93
Initiate Supportive Laboratory Studies	3/94
Initiate Site Evaluation/Assessment	5/94
Complete Collaborative Instrument Arrangements	9/94

1994-95: Finalize with DoD the study and reference site(s), conduct a peer review of the proposed protocol, initiate demonstration level pilots as appropriate, initiate as appropriate full scale field analysis (sample collection, testing etc.). Initiation Date 8/94.

1995-98: Complete data collection on initial study and reference site(s). Initiate data reduction and statistical analysis, initiate preparation (with DoD participation) of study peer review via a workshop presentation format. Prepare final conclusions/recommendations, and for peer reviewed publication of the results.

10. Transition Plan:

DoD/DOE will assist in the selection of priority site(s) for the study and for the chemical characterization of contaminating agent(s) via a survey of prior DoD/DOE-funded and completed descriptive and analytical efforts. The target species will be identified in the impacted ecological community, and a control population will be identified at appropriate reference site(s). The testing chronology will be defined and coordinated with restoration activities. Biomarker matrix endpoints will be identified based on expected site impacts and via experience with previous industrial studies. In start-up phase validation of the sampling strategy, validation of assays, establishment of baseline reference ranges and quality assurance measures will be verified and reported to DoD. In the initial comparative phase the sampling, assay data collection, and comparative analysis of impacted versus reference sites will be conducted and reported to DoD and the feedback will drive corrective action(s) in conformance with quality assurance standards. Finally, the evaluation phase will cover statistical analysis, peer review and preparation of a final report to DoD.

All of the above phases will require close consultation and coordination with DoD personnel in charge of the sites studied. Such communications will be both verbal as well as in the from of quarterly progress reports issued by the offeror.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	FY00
SERDP	900	800	700	700	700	700		
USEPA	--	100	200	200	200	200		

12. Performers:

Ecological Monitoring Research Division (EMRD), Environmental Monitoring Research Laboratory (EMSL), U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268; U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010; U.S. Army Research Development and Engineering Center, Aberdeen Proving Ground, MD 21010.

13. Principal Investigator:

F.B. Daniel, PhD. Director,
Ecological Monitoring Research Division
26 W. Martin Luther King Drive
Cincinnati, OH 45268
Phone: (513) 569-7401
Fax: (513) 569-7609

14. Keywords:

Ecological Biomarkers, Ecological Risk Assessment, Exposure/Effects Assessment, Munitions, Site Assessment, Wildlife Protection

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Genetic Diversity Monitoring in Plants and Wildlife

3. **Agency:** U.S. Environmental Protection Agency

4. **Laboratory:** Environmental Monitoring Systems Laboratory

5. **Proposal ID:** #246

6. **Problem Statement:**

Goal: The goal of this project is to monitor the genetic diversity of feral populations in ecologically sensitive areas using DNA fingerprinting technologies. Loss of diversity resulting from habitat destruction and pollution is a major concern in wildlife populations. The genetic diversity or total gene ensemble of a population reflects its intrinsic robustness. Loss of genetic diversity leaves a species less able to adapt to new environmental stressors; therefore, loss of population genetic diversity can foreshadow species loss, with resultant loss of biological diversity within an ecosystem.

Background: Undisturbed natural populations tend to maintain a high degree of biological diversity or polymorphism, but any environmental stress that eliminates a large fraction of individuals from the breeding population can eliminate (by pure chance) important genetic variants. This phenomenon, known as a genetic "bottleneck", leads to a reduction of heterozygosity in succeeding generations. The overall effect is populations with greater vulnerability to future stresses. Therefore, quantitative measures of genetic diversity can be useful as indicators of past environmental insult as well as criteria for targeting potentially sensitive, i.e., genetically homogeneous populations.

Measurement of population genetic diversity directly supports the SERDP Conservation thrust area as an assessment tool to identify vulnerable populations and subpopulations of many species of animals and plants, and to monitor their responses to ongoing conservation and protection efforts. This project will have both basic research and applied research components. Enhancement of fingerprinting technologies and statistical evaluations will continue, especially as new species are examined. Once the analytical strategy for a species or genus is established it will be applied to a myriad of situations confronting member populations. This proposal is for continuation and enhancement of the efforts to develop fingerprinting technologies as genetic diversity measures currently underway in this laboratory with SERDP support.

7. **Project Description:**

Technical Objectives: The technique of DNA fingerprinting is being widely used to determine the identity and relatedness of individuals (particularly humans), and is also attracting attention as a tool for assessment of genetic variations within and between populations. Genetic distinctions between individuals will be demonstrated by analyzing unique differences in DNA, even in species that are otherwise genetically uncharacterized. The summation of DNA fingerprint differences of many individuals will provide a measure of genetic diversity in the population from which those individuals are derived.

Technical Approach: In this laboratory, we are currently adapting two different, but complementary, fingerprinting techniques for use in several species of fish and terrestrial animals. The first method relies on the presence of short repetitive DNA sequences interspersed throughout the genomes of most organisms. These DNA sequences, called VNTRs (variable number of tandem repeats), exhibit high variability within a population. Bands visualized on a Southern blot of target genomic DNA, using radiolabeled probes specific to the repeat sequence, are the genetic identity of an individual. Comparison of the banding patterns among individuals from a population yields a measure of genetic variation within that population. Comparisons across populations yield measures of relative genetic variation and also of the degree genetic relatedness of the populations. This method is being applied to a test sample of DNAs purified from more than seventy individual brown bullhead catfish representing three populations from both environmentally impacted and clean areas.

The second fingerprint method is based on thermal cycle polymerase chain reaction (PCR). In this procedure, DNA marker bands are biochemically multiplied by a cyclical enzymatic reaction with target DNA. This amplification process occurs when synthetic 10-base DNA molecules, used in the reaction, match exactly with regions in the DNA of interest. This is termed DAF, or DNA Amplification Fingerprinting. DAF reactions, for each of 400 commercially available synthetic 10-base molecules, yield several distinct bands or amplification products - depending on the species surveyed. These products (≤5,000 base pairs) from PCR reactions are visually analyzed by gel electrophoresis in agarose or polyacrylamide. Genomic DNA from two individuals within a species often produce disparate amplification banding patterns. A particular DNA band which is generated from the genome of one individual, but absent in a second individual, represents a polymorphism which can serve as a genetic marker. These markers, presumed to be allelic, are inherited in a Mendelian fashion. By statistically analyzing the segregation of these marker among the progeny of a sexual cross, or individual members of a population, genetic maps and indices of heterozygosity of virtually any species can be assembled.

Also, we have developed an ecologically based method of tissue/DNA acquisition for direct use in DNA Amplification Fingerprint reactions. This simple and rapid technique, which is non-intrusive to terrestrial and aquatic animals, obviates need for radionuclides and isolation, purification, and quantitation of genomic DNA for thermal cycle amplification reactions. This method combines the powerful tools of genetic analysis with an ecologically favorable means of sample acquisition. The strategy is particularly useful when collecting field specimens for population or forensic analysis, or species verification on field specimens and endangered species.

Using the raw fingerprint data from both of these methods, several mathematical treatments for assessing DNA fingerprint diversity are being examined and compared in order to determine the best statistically valid approach. This part of the effort is being done in conjunction with Dr. Vicki Hertzberg with a Cooperative Agreement funded by SERDP.

Since methods of DNA fingerprinting are under continuous and rapid advancement within the scientific community, we are requesting continuing SERDP support for development of the most efficacious system for each new species to which population genetic diversity measures are applied. Most particularly we will be expanding our efforts to examine plant population genetics. We intend to use an expanding battery of VNTR probes, such as PCR generated synthetic tandem repeat (STR) probes. We intend to adapt the new non-isotopic probe labeling techniques for use with our fingerprinting methods, which would avoid the use of radioisotopes,

providing the advantages of standardization due to a long probe shelf-life and portability of methods to laboratories not equipped for radioisotopes usage.

We also will require continuous statistical support in order to tabulate and analyze data generated as each new population and species is examined but to continue to develop and refine the statistical methods required. Each new species will present not only a unique set of banding patterns to be analyzed, but these analyses will need to take into account characteristic higher-order population dynamics, most notably differences in breeding strategies.

We expect ever-increasing liaison with field ecologists who are experienced with and possess detailed knowledge of each relevant population. When appropriate, these interactions will be formalized as cooperative agreements. This will provide detailed expertise and assistance in field sample collection.

These fingerprint measures of population genetic diversity will directly support the conservation efforts of DoD/DOE by providing assessment tools for monitoring, protecting and rehabilitating natural ecosystems.

8. Expected Payoff:

This method will provide a rapid, non-invasive, and cost effective monitoring method in the form of an assessment of population genetic robustness for virtually any species, animal or plant, aquatic or terrestrial. It is anticipated that it can be modified into a commercially available, field usable tool and marketed via a CRADA.

9. Milestones:

1.	Development and validation of methods	FY94-95
2.	Development of DAF method - journal article	FY94
3.	Statistical methods in place, developed under cooperative agreement	FY94
4.	Statistical methods demonstrated with three fish populations - publication	FY94
5.	Explore methods for plants via cooperative agreement or interagency agreement	FY94-95
6.	Applications of developed methods to field situations - collaborative efforts with other researchers - results reported as journal article	FY95-96
7.	Demonstration of DAF method as applied to feral voles	FY94-95
8.	Transfer of methods to other agencies and the private sector via IAG and/or CRADA	FY97
9.	Comparison of VNTR and DAF methods across 3 populations - publication	FY95

10. Transition Plan:

We anticipate the development of a set of user-friendly standard field methods for monitoring population robustness that could be transferred to the individual end user or to centralized facilities which would run service samples for the end users. We expect these methods to be potentially marketable via a CRADA.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	200	200	200	200	200	1000

12. Performers:

U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati, Ecological Monitoring Research Division, Annette C. Roth, Ph.D.; Oak Ridge Institute for Science/Education by Interagency Agreement, David L. Lattier, Ph.D.; Department of Environmental Health, University of Cincinnati, by Cooperative Agreement, Vicki Hertzberg, Ph.D. (Statistical Methods) to be named: by Cooperative Agreement, to explore plant DNA fingerprinting; Biomedical Research and Development Laboratory, Ft. Detrick Department of Army, Dr. Hank Gardner, Dr. E. Baumel by Interagency Agreement Additional Cooperative Agreements.

13. Principal Investigator:

Dr. M. Kate Smith
USEPA
Ecological Monitoring Research Division
Environmental Monitoring Systems Laboratory
26 West Martin Luther King Drive
Cincinnati, OH 45268
TEL: (513) 569-7577
FAX: (513) 569-7609

14. Keywords:

DNA Fingerprinting, Ecological Monitoring, Genetic Diversity Measures, Heterozygosity Indices, Polymorphism, Population Genetics

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Marine Mammal Health Monitoring

3. **Agency:** Navy

4. **Laboratory:** Naval Command Control and Ocean Surveillance Center, RDT&E Division (NRaD), Code 51

5. **Proposal ID:** #050

6. **Problem Statement:**

The effect of estuarine, coastal, and ocean pollution on the high visibility upper food-chain predators, the cetaceans (whales, dolphins, porpoises), is poorly understood. Information by which to gauge pollution effects is not available. The goal of this project is to employ Navy capabilities and experience to enhance marine mammal conservation, identify opportunities for the wider use of Navy expertise in marine mammal health and physiology, and develop information on baseline values on pollutants and disease. We will employ specialized expertise and unique marine mammal collections and data at the Naval Command Control and Ocean Surveillance Center, Research and Development Division, (NRaD) for improvement of knowledge of marine mammal biology to assist in marine mammal conservation and to provide potential sensitive indicators of pollution and disease in the natural ocean environment.

Dramatic die-offs among several marine mammal populations worldwide has triggered questions regarding possible links with industrial, military, and recreational alterations of marine ecosystems. A major case in point is the great public attention and controversy related to the die-offs of dolphins on the East and Gulf coasts of the U. S. in 1987-89, in the Persian Gulf in 1986, and on the coasts of France and Spain in 1990. In all of these incidents, pollution was initially blamed. The 1986 event was not investigated thoroughly enough to make any conclusions as to cause since only four of more than 500 dead animals were examined. The later die-offs were much more thoroughly studied and implicated natural toxins, extreme climatic conditions, or disease as the cause.

High levels of some pollutants were found in many of the dead dolphins. Some environmentalists and environmental scientists maintain that these toxic agents were indeed the underlying cause of the die-offs. Significant mortalities have included harbor seals (Phoca vitulina) in the North and Baltic Seas, the striped dolphin (Stenella coeruleoalba) in eastern North Atlantic and Mediterranean waters around France, Spain and adjacent regions and the Atlantic bottlenose dolphin (Tursiops truncatus) along the eastern and Gulf coasts of the United States. Investigations surrounding these events have emphasized the complex nature of their occurrence and such etiologies as natural infectious agents, biological toxins and environmental contaminants or a combination of such factors are being examined as responsible agents. All have generated considerable concern about the degree to which higher vertebrates may serve to monitor the environmental health of oceans, ports, and harbors.

Marine mammals feed high on the food chain and can serve as ultimate bioaccumulators of a variety of marine contaminants. Because these mammals tend to be long-lived and because such

toxicants as heavy metals generally have lengthy half-lives in biological systems, accumulation can continue over many years, magnifying the levels and potential impacts of pollutants within animal tissues. Since virtually any marine species will have incorporated at least some contaminants, it is no longer a question of determining whether or not a species harbors contaminants, but rather of clarifying at what level such pollutants exist and in what quantities they can be tolerated before posing a health liability to their host.

However, the issue of harmful levels is complicated by numerous variables which must be recognized for realistic evaluations. There are not only many types of pollutant categories (such as heavy metals, organochlorines and petroleum hydrocarbons) but their respective behaviors within the body can vary with contaminant type and with animal species. Also, a given contaminant may occur in different molecular combinations. For example, mercury can be incorporated in elemental form or it may be complexed to various organic moieties, as in the formation, for example, of methylmercury which is much more toxic than elemental mercury in isolation. Also, certain heavy metals interact so that the combined presence of some (such as mercury and selenium) will affect the severity of associated toxicities. Various pesticides, though toxic, may become even more hazardous as they are metabolized into intermediary compounds while the body attempts to process them for elimination. This last effect is further complicated by the fact that specific degradation products will vary with animal species since species differ in the cellular enzyme systems available for processing the original toxin. The age of the animal is also a factor since older animals may, in some cases, have higher levels of contaminants due to life-long accumulations. The sex of the animal and sexual cycle phases must also be considered. Certain contaminants (such as some heavy metals) may be transferred across the placenta to the fetus during gestation; other contaminants (such as pesticides) are also mobilized from the female during lactation and transferred to her offspring through milk. Accordingly, a very young animal can actually have higher levels of some pollutants than the mother who is many years older.

This project was identified in the Department of the Navy Environmental Strategic Plan in 1991. One listed objective was to "identify opportunities for the wider use of Navy expertise in marine mammal health and physiology." The project was approved for funding in FY93. This proposal is for continuing funding of a previously approved and funded project initiated under the FY93 SERDP program.

7. Project Description:

The Navy Marine Mammal Program based at NRaD has developed special expertise in marine mammal health and physiology during the past 30 years. NRaD maintains 100 bottlenose dolphins with origins (1st or 2nd generation) in the Gulf of Mexico. The dolphins are of both sexes with a wide range of age from immature through mature, and older animals. These dolphins were collected over the past 30 years or born during that time at NRaD. Though they are genetically similar to their wild relatives in the Gulf of Mexico, the Navy dolphins have been fed fish and squid from other sources, primarily from the North Pacific ocean. Therefore, the Navy dolphins constitute a good control group for comparing both direct environmental pollution and food-borne or food-web concentrated pollution.

The Navy conducts complete physical examinations at six-month intervals. Therefore, consistent health records are available on each individual which chronicle much medical and physiological information that can be used in the proposed study. The animals, the data base, and the special expertise at NRaD could be utilized to enrich the health of the marine environment through

development of data and methods by which the natural populations of bottlenose dolphins, other marine mammals, and possibly other large marine species could be assessed. Wildlife management officials will have better information with which to formulate decisions about marine mammal conservation. Furthermore, this data will also have the potential to reveal sensitive bio-indicators by which the status of the ocean environment can be further evaluated.

The marine mammal data base on animal health and physiology at NRaD will be reviewed, analyzed and data published correlating values with biological characteristics of animals such as sex, morphometrics, and age. Without the Navy records, only a small amount of these data is currently available. Serial measurements will be made of different blood and plasma components to determine which constituent offers the most consistent and reliable values in the assay for a selected list of pollutants and diseases. Serial measures will also be taken from blubber biopsies for correlation with the most consistent blood measures and with the same biological characteristics mentioned above. No additional animals will be required and no additional manipulation of marine mammals will be necessary for these studies. All of this information will be collected during procedures mandated under the health maintenance program. Numerous additional tests and modern procedures will be carried out with the materials already collected from Navy marine mammals. Publication of this new information will serve as an invaluable reference for evaluating individuals in wild populations and especially will help in elucidating future die-off diagnosis and prospective courses of action. This data will also have the potential to identify ocean pollution as concentrated in marine mammals because it will provide the basis for comparison with similar data collected from animals from wild populations.

Another factor that is unknown at present, and which must be understood, is the effect of various marine pollutants and biological characters (e.g. sex, age, body conformation) on the immune systems of cetaceans. The root cause of some die-offs have been suspected immune system deficiencies. Our laboratory is currently generating dolphin and whale monoclonal antibodies against CD3 (a pan T-cell marker), CD4 (a T-helper-cell marker), CD8 (a cytotoxic T-cell marker) and immunoglobulins (IgG, IgM, IgA). The development of these markers will enable us to assess T and B cell compartmentation in the lymphoid organs that are the foundation of the immune system (spleen, thymus, lymph nodes, tonsil, gut-associated lymphoid tissue, mesenteric lymphoid masses). While the morphology of these organs has been studied by our collaborator (Romano, 1993. J. Morph), the positive identification of T and B cells has not been possible due to lack of cetacean-specific markers. Positive identification of lymphocyte subsets will also reveal the cell types with which postganglionic sympathetic nerve fibers associate, thus establishing an anatomical link between the nervous and immune system in cetaceans. In our inventory are lymphoid organs from stranded and sick cetaceans as well as healthy animals collected in sanctioned hunts by native people which can be compared using developed markers. Further, we will be able to identify lymphocyte subsets in the circulating blood of living animals as an aid to health assessment. Thus, we will be able to evaluate the immune system more directly for the first time.

This proposal addresses requirements identified in the Tri-Service Environmental Quality R&D Strategic Plan under Conservation Thrust 4Q (T/E Species Management, Propagation, and Recovery).

8. Expected Payoff:

More information and technology will be available for assessment of all human impacts, including DoD impacts on die-offs of dolphins in the coastal areas of the United States and elsewhere. Stewardship of these high-profile marine resources will be enhanced. Reports listing critical criteria will be distributed to stranding networks and cognizant government agencies at all levels. Managers will have a better information base from which to make decisions about trade-offs between economic, military, and environmental concerns.

9. Milestones:

1.	Complete archive specimen analysis	12/94
2.	Protocol for immune assessment marker development	01/95
3.	Report on milk, tissue, and formed blood cell elements	08/95
4.	Report on T-cell markers	11/95
5.	Draft reports from the data base assessment relative to physiology and health completed	12/95
6.	Reports from the data base assessment relative to physiology and health will be published and distributed to user agencies	10/96
7.	Report on immune system correlates and bioaccumulation	06/97
8.	Distribute all published reports to user agencies and groups	09/97

10. Transition Plan:

Marine mammal protection agencies at local, state and national level are identified including the Marine Mammal Commission, the U. S. Department of Agriculture, and the National Marine Fisheries Service. Stranding networks exist along most coastal areas of the United States. Information from this work will be distributed to these users as well as to the general scientific community and applicable Navy commands and units.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	249	250	252	254	1005

12. Performers:

Government: Naval Command Control and Ocean Surveillance Center, RDTE Division, Biosciences Division, Code 51, San Diego, CA 92152.

Industry: Science Applications International, Marine Division, 3990 Old Town Avenue, San Diego, CA 92110., through contract with NRaD.

Academic: Department of Anatomy and Public Health, College of Veterinary Medicine, Texas A&M University, College Station, TX 77843-4458.

Certain specialized tests will be contracted with other agencies such as National Animal Disease Laboratory, Toxicology Branch (Ames, IA), the Geochemical and Environmental Research Group (GERG) of Texas A&M University (College Station, TX), the Department of Veterinary Pathology of the Armed Forces Institute of Pathology (AFIP).

13. Principal Investigator:

Dr. Sam H. Ridgway
Naval Command Control and Ocean Surveillance Center (NCCOSC)
RDTE DIV (NRaD) 5107B
49620 Beluga Road, RM 200
San Diego, CA 92152-6266
Tel: 619 553-1374
Fax: 619 553-1346

14. Keywords:

Cetacean, Pollution, Disease, Hematology, Immune, Bioaccumulation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Conservation

2. **Title:** Strategy for Resource Management on DoD/DOE Lands Combined with Decision Support for Disturbed Ecosystem Renewal

3. **Agency:** Department of Energy

4. **Laboratory:** Oak Ridge National Laboratory

5. **Proposal ID:** #758

6. **Problem Statement:**

U.S. Department of Defense (DoD) and U.S. Department of Energy (DOE) lands are subjected to a wide variety of uses ranging from military training to hazardous waste disposal to timber production. Nevertheless, these lands are often the last large natural areas in otherwise developed environments. As such, many natural and cultural resources have been preserved, and site with these attributes can be used as reference sites for conservation, rehabilitation and mitigation efforts at disturbed sites. For example, the DOE National Environmental Research Parks (NERPs) can provide long-term natural resources data useful for rehabilitating similar DoD and DOE sites where access is limited. The long-term DOE Parks data on various biotic properties have significant value for developing and validating models and management schemes.

Currently, there is no unifying framework for managing these lands that provides decision makers with a consistent approach to balancing the goals of DoD and DOE operations with the need for resource conservation. We propose to develop and demonstrate such a framework. Our strategy is to use existing data and state-of-the-art technology, with an emphasis on Geographic Information Systems (GIS) and computer modeling, to characterize the natural and cultural resources on selected DoD and DOE sites. We will develop and demonstrate advanced computer-based models to predict incremental and cumulative impacts of agency activities on habitat, biodiversity and cultural resources and to find solutions that maximize mission-oriented use of the lands while sustaining long-term ecological diversity and preserving cultural resources. The demonstration will involve model predictions of biodiversity subsequent to specific land use activities as compare to in situ measures after such manipulations on DoD or DOE lands.

The proposed strategy characterizes resources in a risk assessment framework to provide support for DoD and DOE land management that is applicable to levels of organization ranging from species to ecosystems. By risk assessment, we mean to estimate the probability of undesirable (or desirable) outcomes of land management activities in a spatially explicit fashion. The framework will provide agency decision makers with a tool for evaluating the effects of alternative land management activities on natural and cultural resources. The model will be useful to land/facility managers and planners for addressing questions such as: What is the relative risk to biotic and/or cultural resources of a set of potential land-use activities? Across a set of potential sites, where would an activity best be placed to minimize the effects on biotic and/or cultural resources? What remedial actions would provide the maximum conservation benefit? What are the impacts on habitats or species of changing the frequency or impact of

training exercises at a site? Although the proposed study is a new program in basic research, it will build upon existing data for DoD and DOE lands.

7. Project Description:

We propose to develop an innovative, spatially-explicit decision model that will be used to assess the impact of DoD and DOE activities on natural and cultural resources. It will focus on the loss/alteration of habitat and the resulting impact on biodiversity. Agency land-use activities will be characterized using a common set of parameter (magnitude, frequency, areal extent, spatial distribution, predictability) that can be applied both to alternative activities and different levels of the same activity. This framework permits the incremental and cumulative effects of diverse activities, such as road building, military maneuvers, grazing, timber harvests, and environmental restoration, to be evaluated. Evaluating the risk posed to habitats, species and cultural resources is expressed as the probability of a decline or enhancement in the abundance of guilds of species or cultural features. Although the framework is generic, with appropriate databases it can be applied to any site.

Model development will focus initially on two case studies consisting of paired DoD/DOE sites where each pair is within the same physiographic region. The case studies represent two biomes: 1) eastern deciduous forest, which will include the Oak Ridge Reservation (ORR), Tennessee (DOE) and Ft. Knox, Kentucky (DoD); and 2) semi-arid shrub steppe, which will include the Hanford Reservation, Washington (DOE) and the Yakima Training Center (YTC), Washington (DoD). Choice of which study area to be used as the first test of model predictions will be based upon discussions at the first of two workshops. The first field test\demonstration will begin in 1995 and the second will occur in 1996. The field test\demonstration will consist of model predictions of biodiversity alternations from a particular land management practice (e.g., forest clearing, grazing, training exercise, etc.). Then the management practice will be applied to a site and the biodiversity before and after the manipulation will be compared to model predictions. These will be field experiments that will be used to test the models. The two pairs of DoD and DOE test sites are sufficiently different to be able to test a range of management practices.

The Oak Ridge Reservation and Ft. Knox respectively encompass 14,000 and 44,700 ha of eastern deciduous and coniferous forest. Large blocks of land have been cleared for low-level radioactive-waste disposal areas on ORR while tank training at Ft. Knox (Ft. Knox's main mission) has denuded scattered blocks of land. The DOE Hanford Reservation and the DoD Yakima Training Center respectively encompass 145,600 ha and 105,800 ha of semi-arid shrub-steppe vegetation dominated by sagebrush/bluebunch wheatgrass. Environmental cleanup activities threaten large tracts of high quality sagebrush community at Hanford while the Army's need to increase heavy mechanized equipment training at YTC poses a similar threat there.

The proposed project supports both DoD regulations and DOE orders (e.g., A. F. Regulation 126-1, Conservation and Management of Natural Resources, DOE 4320.1B, Site Development Planning) that establish policies for managing and conserving natural resources and for site development and land management planning. As our research approach is implemented, two workshops (one at the start of the project and one just prior to developing the risk assessment framework) will be conducted to establish linkages between decision makers and scientists, and a peer review advisory board will be established to ensure that the research is responsive to local needs and consistent with national policies and needs.

Our approach entails five components which integrate existing data, model development and demonstration, and risk assessment.

1) Quantitatively characterize land-use activities. A matrix of characteristics to describe land-use activities on DoD and DOE lands in terms of magnitude, frequency, areal extent, spatial distribution, predictability, and effects on habitat quality and cultural resources will be developed. For example, some types of troop training are low-intensity impacts that are dispersed throughout a site, whereas construction of an industrial facility is a high-intensity activity that occupies a limited area. To assure representation of the selected activities and relevance to each agency, the matrix development will entail a workshop involving representatives from DoD and DOE sites.

2) Develop a land-cover change risk model. A spatially-explicit, land-cover change model will be developed to simulate potential changes in or loss of individual cover types in response to the land-use activities. Inputs to the model will include the matrix of parameters describing land-use activities, and gridded (digital raster) maps of site characteristics, such as present land cover, slope, aspect, soils, etc. The model will simulate the impact of land use activities on land cover. The model will be probabilistic so that stochastic aspects of the land-use activity (e.g., the frequency of training maneuvers) or it effects on the habitat (e.g., the degree to which a forest is damaged by artillery fire) or cultural resources can be represented. Land-use activities that are relatively deterministic and depend on the suitability of the land (e.g., location of new runways) also are easily accommodated within a probabilistic model by setting the appropriate probabilities to 1.0 and fixing specified parameters. From the model, tables and maps of potential land-cover change due to land use activities will be produced for a particular site. The land-cover change projections will be developed for different scenarios of land-use activities and land cover patterns. Stochastic simulations with the model can be replicated many times and the results summarized statistically, thereby providing an estimate of the magnitude and range of potential effects. Most importantly, the stochastic but mechanistics nature of the modeling will allow us to quantify the probability of specific land-cover changes taking into account known uncertainties.

3) Develop a resource-susceptibility model. The second model to be developed will relate characteristics of species, ecosystems, and cultural features to land-cover patterns resulting from land-use activities, as projected by the land-cover change model. Development of this model will evolve from discussions at a workshop involving DoD and DOE land managers. Long-term NERP data will be especially important in the model development. This resource model will match land cover characteristics (e.g., frequency of land cover types, abundance of suitable habitat, size of habitat patches, frequency of edges, corridors, etc.) to species and ecosystems characteristics (e.g., home range size, vegetation patterns) and to cultural features. For example, activities that cause habitat fragmentation will be detrimental to species that require large blocks of contiguous habitat (e.g., forest-interior species). This model will be probabilistic to ensure its compatibility with quantitative risk assessment. Potential effects on species and ecosystems of no management, alternative land-use activities, environmental restoration, or natural events can be examined. The probability of an undesired or desired outcome (such as loss or increase of a population of interest) is estimated by Monte Carlo simulations of the models under particular scenarios and examination of the frequency distribution of outputs. The visualization that will accompany this spatially-explicit model will also permit managers to "see" the effects of alternative activities on populations or cultural features of interest.

4) Use case studies to field test the modeling approach. The model will be tested by applying it to the paired DoD and DOE sites (Oak Ridge Reservation/ Ft. Knox and Hanford Reservation/Yakima Training Center). To the extent possible, existing land-use/land-cover and resource maps will be used, however some map development may be required. Data available on highly impacted or inaccessible DoD sites can be augmented by the extensive historical data available for the DOE NERPs. Spatial data for each site will be compiled in grid-cell (raster) format into a Geographic Resource Analysis Support System (GRASS), developed by the U.S. Army Corps of Engineers (Construction Engineering Research Laboratory, Champaign, Illinois) GIS (all spatial analyses will be done in accord with the guidelines of the Federal Geographic Data Committee). Converting the existing and acquired information on land-use/land-cover and cultural and natural resources to a GRASS format will assure its compatibility with the land-cover change and resource-susceptibility models. The goal of these case studies is to apply the conceptual framework (i.e., use of the land-use activity matrix, the land-cover change model, and the resource-susceptibility model) to specific sites. For example, collaborators at Pacific Northwest Laboratory will develop a rangeland ecosystem model that incorporates disturbances from military training exercises and environmental restoration options for YTC. This model will i) identify locations to be impacted by training, ii) quantify ecosystem impacts of training, and iii) estimate the economic costs and effectiveness of various environmental restoration activities. Simulations will be conducted for single and combined land-use activities that might occur at each site, and the probability of undesirable or desirable changes in habitats or species will be projected in map and tabular form. To the degree that suitable data are available, predictions will be compared with field data. Biodiversity data collected before and after specific land use activities will be used to test predictions.

5) Conduct risk assessment. A final workshop involving land managers from DoD and DOE sites will be held to consider the applicability of the proposed framework to evaluating risk to biodiversity and cultural resources associated with specific land management practices. The workshop will build upon EPA's Ecological Risk Framework and consider how our model framework contributes to estimation of land-management risks.

8. Expected Payoff:

This research will provide a rigorous, quantitative method for conserving and enhancing biodiversity and cultural resources while conducting activities necessary for DoD and DOE missions. The results will include:

1) a general risk-based framework that can be used by DoD and DOE land managers and site development planners to analyze the potential impact of selected land-use activities on natural and cultural resources.

2) case study results including tabular projections of percent change in cover and distribution of habitats, species guilds, and cultural features for various land management and site development scenarios at the case study sites along with maps of potential risks to different land cover types under the specified land management scenarios.

3) a user-friendly version of the land-cover susceptibility and species-susceptibility models that could be applied at various DoD and DOE sites.

In addition to its use for management of natural and cultural resources, the proposed research is directly applicable to 1) planning for facility closures and realignment (e.g., identification of

facility closures that provide the best conservation opportunities), 2) developing environmental restoration and waste management strategies, 3) supporting compliance with the Endangered Species Act, the National Historic Preservation Act, the National Environmental Policy Act, and the Executive Orders for Floodplains and Wetlands, and 4) developing integrated risk assessments that address cumulative effects.

9. Milestones:

1.	Land-use activities workshop	11/94
2.	Report on land-use activities workshop	2/95
3.	Plan for field test\demonstration at first site (either deciduous forest or the semi-arid shrub steppe)	4/95
4.	First field test	5-9/95
5.	Report on land-cover change risk model	6/96
6.	Plan for field test\demonstration at second site (either deciduous forest or the semi-arid shrub steppe)	4/96
7.	Second field test	5-9/96
8.	Report on natural resources susceptibility model	12/96
9.	Report on framework for land management	4/97
10.	Analysis of field tests\demonstrations on land-use impacts to sites	2/98
11.	Risk assessment workshop involving land managers from DoD and DOE sites	4/98
12.	Report on risk assessment framework	6/98
13.	User-friendly computer code for applying framework	6/98
14.	Technology training session for DoD and DOE land managers	9/98

These milestones assume a starting date of June 1994.

10. Transition Plan:

User-friendly codes of the models and land-use management framework developed in this proposal will be transferred to DoD and DOE land managers and site development planners. The inputs of DoD and DOE land managers will be obtained throughout the proposed work via their participation in workshops and on the peer review advisory board.

11. Funding: ($K)

FY94	FY95	FY96	FY97	FY98	TOTAL
500	1000	1006	616	0	3122

12. Performers:

The DOE NERPs (Nevada Test Site, Idaho National Engineering Laboratory, Savannah River Ecology Laboratory, Pacific Northwest Laboratory, FermiLab/Argonne National Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory) and selected DoD facilities (Yakima Training Center, Ft. Knox, Construction Engineering Research Laboratory and others) will participate in the two workshops, Oak Ridge Reservation, Ft. Knox, Hanford Reservation, and Yakima Training Center will participate in the field case studies. This proposal includes

funds for workshop participation by DoD/DOE land managers, planners and scientists and for each installation involved in the case studies.

13. Principal Investigators:

Virginia H. Dale
Oak Ridge National Laboratory
Bethel Valley Road, P.O. Box 2008
Oak Ridge, TN 37831-6038
TEL: 615 576-8043
FAX: 615 576-8646

Ronald N. Kickert, K6-63
Battelle Pacific Northwest Laboratory
P.O. Box 99
Richland, WA 99352
TEL: 509 372-0814
FAX: 509 376-3968

14. Keywords:

Biodiversity, land use, habitat, ecological risk, site development planning, species guilds

TABLE A-IV **FY 1994 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS**	**Funding ($K) FY94**	**ID Number**	**Page Number**
Energy Conservation			
Low Energy Model Installation Program (A)	1,650	639	A-309
Natural Gas Based Air Conditioning Demonstration (A)	230	643	A-313
Advanced Cogeneration and Absorption Chilling (DOE)	300	599	A-316
Optimize Energy Efficiency of AC Induction Motors (EPA)	250	231	A-321
Renewable Energy			
Fuel Cells for Military Applications (A)	350	641	A-326
Advanced Cycle Mobile Heat Pump (AF)	850	94	A-329
Thermal Acoustic Piezoelectric Power Generator (DNA)	100	84	A-331
Geothermal Space Conditioning for Large DoD Buildings (DOE)	800	580	A-333
Clean Liquid Fuel from Biomass and Carbonaceous Wastes (EPA)	500	210	A-338
Utilization of Biomass Technologies on Military Installations (EPA)	750	227	A-343
Low Emissions Shipboard Fuel Cell Power Plants (N)	600	47	A-346
Photovoltaics for Military Applications (N)	4,000	46	A-351
Energy Conservation/Renewable Resources Total	**10,380**		

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Low Energy Model Installation Program

3. **Agency:** Army

4. **Laboratory:** CERL

5. **Proposal ID:** #639

6. **Problem Statement:**

Current energy policy requires federal and DoD facilities to reduce energy consumption and costs by 30% from 1985 to 2005, by implementing a variety of project and maintenance strategies, maximizing the use of alternative financing. The Energy Policy Act of 1992 requires that all projects that payback within ten years be completed by 2005. Proper analytical tools and methodologies to ensure optimum implementation of the energy program are not available. The DoD also has no example demonstrating all the strategies simultaneously utilizing existing resources available to the engineer community. The DoD Low Energy Model Installation Program at Fort Hood, Texas, will demonstrate the effectiveness of the comprehensive approach while acting as a testbed for the development and technical transfer of tools and methodologies. This project is a combination of applied research, technology demonstration, and technology transfer. The Low Energy Model Installation Program is a continuing effort which received FY 91-93 funding along with DoD and FORSCOM funding. Continued funding is required to complete generic tool development, develop construction design enhancement methodologies, design projects, and complete energy saving and sustainable development demonstration projects at Fort Hood.

7. **Project Description:**

The Low Energy Model Installation Program is twofold effort. The first technical objective is developing a generic methodology for bringing an entire installation up to an energy efficient state. The second technical objective is to implement this methodology at a given installation for demonstrating and validating the process. The two efforts are being conducted simultaneously in a synergistic manner. SERDP funding is intended to pay for the methodology and tool development, project development, minor demonstrations, and project validation. Once the large projects have been identified and the technology demonstrated, other funds will be used to complete them. SERDP leverages other much larger funding requirements.

The program's technical approach is a step by step logical process, shown below:

(1) tracking and predicting installation energy use
(2) identifying and evaluating energy reduction options
(3) developing phased implementation plans
(4) prioritizing projects and identifying funding options
(5) demonstrating new concepts and technologies
(6) quantifying environmental benefits
(7) developing analysis tools based on the above activities

The development of generic analysis tools is designed to formalize the above process and automate it as much as possible. They will provide the DoD and installations with a consistent method and yardstick for evaluating projects and progress. The program builds upon and enhances previous work by Pacific Northwest Labs in the development of the Federal Energy Decision Screening Model (FEDS) and the previous work by Lawrence Berkeley Labs in the development of End-use Disaggregation Algorithm (EDA). It also compliments the separately funded CERL work effort to develop the Renewables and Energy Efficiency Planning (REEP) model to determine the maximum potential and the environmental benefits of energy conservation in the DoD. The final tool that facilitates the process is the Installation Baseline Energy Analysis Model (IBEAM).

IBEAM enables the energy manager to determine the energy flow and consumption trends on the installation. It uses multiple years' input of salient parameters and energy consumption to build an adaptive model of the installation. The model is the used to define energy flow and uses and predict consumption based on changes in the salient parameters and to gauge actual progress. It also quantifies the environmental benefits of the energy program. REEP is a basic scoping tool to be used for programming energy funding, evaluating potential, and assessing energy projects on a large scale. FEDS is a project development and prioritizing tool. Results of a level-2 FEDS analysis will provide the detailed information for project documentation and submittal for funding. EDA is a process of developing information from which to build and enhance the models.

Once the tools are finalized, the DoD will have its consistent yardstick for developing projects, determining priorities and assessing progress. This ability has been missing from the energy program and has hindered effective application of scarce resources. The demonstrations at the model installation will provide living proof that the methodology works.

Historically, new technology has had an extremely slow penetration into the DoD infrastructure. Typical lag times are up to fifteen years. The reasons for this are multiple; some are as follows: (1) the construction system is extremely bureaucratic and relies on outdated specification packages, (2) nearly all parties involved in the construction process are extremely conservative by nature and tend to do things the way they have always been done, (3) technology transfer within the DoD is not as effective as it could be, and (4) installation personnel are leery of new technology, do not trust it to perform properly, and therefore, actively oppose it in their projects. Demonstrations conducted under this program at Fort Hood are intended to overcome these obstacles and show all parties that the current paradigm needs adjustment and that new technology will benefit the installation and the national infrastructure as a whole from both the energy and maintenance perspectives.

The approach to applying new technology in the program is to do small pilot projects to familiarize personnel with new techniques and equipment. These will be followed-up with large, wide-scaled implementation projects funded by the Energy Conservation Investment Program, Military Construction, the DoD Energy O&M Program, or alternative financing.

8. Expected Payoff:

Fort Hood spends about $23 million per year for facilities energy. Preliminary analysis of the potential savings at the model installation are about 32% of the energy and 24% of the costs. Since the Department of Defense spends about $2.9 billion per year for facilities energy, savings of this magnitude extrapolated DoD-wide are about $700 million per year. There are also

considerable environmental benefits from such energy reductions such as reduced air emissions and their effects on global climate change. Additionally, external societal savings for such a program are about $350 million per year. Expected reductions in carbon dioxide from both reduced gas and electrical usage at the model installation are in the 35% range. Demonstrations conducted under this program at Fort Hood are intended to overcome obstacles preventing use of new technology and concepts such as "green buildings" and show all parties that the current paradigm can be adjusted to benefit the installation and the national infrastructure as a whole from both the energy and maintenance perspectives. Developing effective tools for energy analyses and capital investment strategies will enable installations to determine the optimal projects to achieve lasting savings.

9. Milestones:

1.	Select and evaluate demonstration site	07/92
2.	Evaluate energy use	09/93
3.	Identify and evaluate conservation projects	12/93
4.	Develop comprehensive project strategy	02/94
5.	Establish energy baseline	03/94
6.	Complete first phase personnel training	09/94
7.	Complete first phase project implementation	09/94
8.	Develop tools fot identifying options (FEDS and REEP)	12/94
9.	Develop energy tracking and prediction model (IBEAM)	09/95
10.	Complete second phase project implementation	09/95
11.	Complete scope and design for sustainable neighborhood	09/95
12.	Demonstrate sustainable neighborhood	09/96
13.	Follow construction and evaluate projects	07/97
14.	Evaluate results and transfer technology	09/97

10. Transition Plan:

The results of this program are twofold. The first area is tool and technique development. These will be transferred within the existing structure for energy management within the DoD. The militarized version of FEDS will be incorporated into DOE's training program. The predictor tools and analysis techniques will be incorporated into DoD training programs. The second set of results are the technology demonstrations at the model installation. These projects will fully involve the installation, the local Corps of Engineers District, and the various Corps Centers of Expertise. These results will be transferred using standard DoD methods such as technical reports, manuals, and bulletins. Since the results of the pilot demonstration projects will show that the technology is applicable to virtually all DoD facilities, they will also be incorporated into training and workshops associated with the energy management programs. Successes at one installation make a given new technology acceptable to others. Demonstrations are an effective way to break the continuing cycle of replacement-in-kind with older, less efficient technology even though the old technology was inappropriate, did not persist, and failed. The technologies being implemented under this program are readily available from industry but have not penetrated the DoD market.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	1650	1000	500	500	3650

12. Performers:

This project is being managed and performed by the Construction Engineering Research Laboratories in Champaign, IL. Additional assistance is being provided by the Cold Regions Research and Engineering Laboratory in Hanover, NH; DOE National Labs (Pacific Northwest Laboratory and Lawrence Berkeley Laboratory); the University of Illinois at Urbana/Champaign; the University of North Dakota; Texas A&M University; and various consulting and engineering firms. Huntsville and South Central Divisions of the Corps of Engineers are also program partners.

13. Principal Investigator:

US Army Construction Engineering Research Laboratories
ATTN: CECER-FEM (Mr. Donald Fournier)
PO Box 9005
Champaign, IL 61826-9005
TEL: (217) 373-3393
FAX: (217) 373-3430

14. Keywords:

Energy Conservation, Global Warming, Demonstration, Renewable Energy, Model Installation, Demand Side Management, Sustainable Development, Renewable Resources

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Natural Gas Based Air Conditioning Demonstration

3. **Agency:** Army

4. **Laboratory:** U.S. Army Construction Engineering Research Laboratories

5. **Proposal ID:** #643

6. **Problem Statement:**

Many existing chilled water systems within DoD are old and inefficient. Most use CFCs or HCFCs as the refrigerant and many of these pose an environmental problem by leaking their refrigerant charge. It is becoming expensive to replace CFCs and potential for EPA fines exist when annual leakage rates exceed 15% of the system charge, which is not an uncommon occurrence. Summer air conditioning loads result in an increased peak electrical demand of 30% or more at most installations. This occurs when electricity is the most expensive and electric utilities have the least reserve capacity.

7. **Project Description:**

Air conditioning requirements at DoD facilities typically occur when the electric rates are the highest. The demand portion of an installation's electric bill can exceed 50% of the total bill. State-of-the-art natural gas fired cooling systems, such as absorption and engine driven chillers, can be used to reduce electric demand, provide domestic hot water, operate at high coefficients of performance, and avoid the use of environmentally harmful refrigerants. In addition, shifting of cooling from electric driven to natural gas fired equipment offers a significant reduction in the overall environmental impact of the cooling load.

Hospitals, barracks, and other DoD facilities where large cooling and hot water loads exist may be prime candidates for gas cooling technologies. The FY93 Defense Appropriations Act provided $6 Million of equipment procurement funds to the DoD for "natural gas chillers for the air conditioning of Department of Defense facilities". The FY94 Defense Budget also includes $16,750,000 to continue with this program. However, no funding was provided with which to identify and evaluate potential implementation sites, develop the equipment purchase documentation, supervise equipment installation and acceptance, monitor equipment performance, or document lessons learned to assess the applicability of these technologies within the DoD as a whole. The proposed project is designed to provide field demonstrations of natural gas chillers at DoD installations and to evaluate their overall applicability within the DoD.

The objective of this project is to evaluate the overall applicability of natural gas fired chiller technology within the DoD through a program of field demonstrations.

8. Expected Payoff:

Payoffs from gas cooling come in two forms, environmental and economical. While CFCs are no longer used, HCFCs are still of some concern as a long term solution. Absorption chillers and desiccant dehumidifiers completely eliminate all CFCs and HCFCs. Engine driven chillers typically rely on vapor compression and HCFCs for their cooling process. Current and expected near future equipment costs are somewhat higher than conventional electric driven vapor compression cooling equipment. Therefore areas with large electric - gas cost differentials will initially be targeted for early application in order to minimize the payback period for the incremental cost of the project. Many gas and electric utilities offer rebates, such as on a per ton of installed capacity, in order to 1) reduce peak electric demand, and 2) increase summer gas sales. These rebates can, in some cases more than make up the equipment cost differential. Also, a number of gas utilities offer lower rates for gas cooling. Some applications will allow heat recovery, particularly engine driven chillers, for heating DHW or boiler makeup water. As these applications are identified the cost effectiveness of the system increases. At current equipment costs, modest utility incentives, and gas rates, gas cooling can be cost effective where average electric rates are in excess of $0.05/kWh. These conditions are met at approximately half of the Army installations.

9. Milestones:

1.	Site selection, performance, procurement guidance	03/94
2.	Phase 1 site selection, design	07/94
3.	Procurement & construction activities	04/95
4.	Monitor phase 1 systems for 1 cooling season	10/95
5.	Phase 2 site selection, design	07/95
6.	Procurement & construction activities	04/96
7.	Monitor phase 2 systems for 1 cooling season	10/96
8.	Phase 3 site selection, design	07/96
9.	Procurement and construction activities	04/97
10.	Monitor phase 3 systems for 1 cooling season	10/97
11.	Final documentation and tech transfer	09/98

10. Transition Plan:

The final report will be in the FEAP format, published by CERL, and made available for use by the other military services.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	230	540	540	360	100	1,770

12. Performers:

The lead agency will be the U.S. Army Construction Engineering Research Laboratories. Supporting agencies and organizations include: NFESC, NAVFAC, AFCESA, OACSIM, DOE.

13. Principal Investigators:

Mr. Ralph Moshage and Mr. Gerald Cler
Commander
USACERL
ATTN: CECER-FE (Mr. R. Moshage)
P.O. Box 9005
Champaign, IL 61826-9005
TEL: (217) 398-5544 and TEL: (217) 398-5552
FAX: (217) 373-3430

14. Keywords:

Natural Gas, Chillers, Cooling, Engine, Absorption, Desiccant

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Advanced Cogeneration and Absorption Chilling

3. **Agency:** Department of Energy

4. **Laboratory:** Brookhaven National Laboratory

5. **Proposal ID:** #599

6. **Problem Statement:**

The U.S. military services are the largest single institutional user of district heating and cooling, with over 6,000 miles of pipeline capacity installed on American military bases. The replacement value of this installed equipment has been estimated at $12 billion. There are strong indications that these systems are technologically and economically costly to operate and maintain. Unless new techniques for upgrading the efficiency, economy, and environmental characteristics of these systems are developed in the near future, it is very likely that a number of unfortunate outcomes could occur. These include: greatly increased operation and maintenance costs, increased environmental impacts and even catastrophic failure. One of the best ways of upgrading existing military-base district-heating systems as well as designing new systems for high efficiency, economy and low environmental impact is to employ advanced forms of cogeneration and absorption chilling.

Within this general situation, U.S. Navy bases generally present very favorable conditions for certain advanced forms of cogeneration and absorption chilling technologies. Naval bases tend to have several characteristics that lend themselves to immediate application of cogeneration and absorption chilling systems in the size range considered here: they are relatively compact, they generally utilize district heating, they have high electric air-conditioning loads, they have a need to phase out chlorofluorocarbon (CFC) refrigerants, and they often experience high electricity costs. These needs can be effectively addressed through the development of advanced cogeneration and absorption chilling technology such as that proposed herein by Brookhaven National Laboratory (BNL) in cooperation with the Naval Facilities Energy Command, for demonstration on bases of the U.S. Navy.

At present, the cogeneration and absorption chilling technology which occupies the market niche between about 100kW and 5 MW is not cost competitive; moreover, it is insufficiently reliable for military applications and it is also environmentally unacceptable. Yet, it is precisely within this range that U.S. Naval bases have the greatest need for cogeneration and absorption chilling technology. BNL proposes to overcome the problems by building on current technology to develop and demonstrate for the Navy a new generation of highly advanced, economical, reliable and environmentally clean cogeneration and absorption chilling systems.

The end product of the proposed four-year RD&D program will be several advanced cogeneration and absorption chilling systems which will be able to meet the needs of naval bases for cost-effective electricity, heating, and cooling for individual buildings, groups of buildings and entire bases. The scale of individual units which are proposed for development range in size between 85 kW of cogeneration capacity and 17 tons of absorption chilling capacity to 750

kW of cogeneration capacity and 350 tons of absorption air conditioning capacity. Modular systems can then be mixed and matched with building and base electric, space-heating and space-cooling loads to meet any load in this range up to 5 MW of cogeneration capacity and 2,300 tons of absorption chilling capacity.

The cogeneration technology which BNL proposes for development will utilize an advanced form of dual-fueled (80% natural gas, 20% diesel oil) diesel engine cogeneration that is characterized by very high energy-efficiency (40% electric, 90%+ overall thermal recovery); high reliability; low installation costs; low maintenance costs; automated operation; and low emissions. The absorption chilling systems that BNL proposes for development will similarly be the lowest-cost and highest-efficiency systems on the market, since these systems are intended to be powered by inexpensive cogenerated waste heat.

The project will address three research categories: applied research, technology demonstration, and technology transfer. It builds on previous work done by BNL for the Department of Energy (DOE).

7. Project Description:

The following outlines a proposal for the development of advanced cogeneration and absorption chilling at BNL. It includes the development, testing, and demonstration of an advanced diesel cogeneration package, the advanced absorption chiller, and a cost-efficient means for mitigating diesel engine emissions with emphasis on oxides of nitrogen. A four-year program is envisioned, costing $950,000 per year. The individual tasks with this program are described below.

FY 1994

Task 94-1. Complete Development and Test of Advanced 85 kW Cogeneration Packaged System ($250K)

The cogenerator will use a dual-fueled diesel engine fired by 20% oil and 80% natural gas. The major advantages of this approach to cogeneration are system reliability and low cost consistent with high reliability. Electrical efficiency will be 40% or greater with overall thermal recovery of 90% to 96%. It will employ condensing exhaust to maximize thermal recovery and achieve low emissions. The vertical configuration of the system and low manufacturing costs will keep installed costs low - $750/kW. The system will be controlled electronically, with artificial intelligence routines to predict and identify maintenance needs, thereby greatly reducing unscheduled downtime and significantly increasing reliability. Maintenance costs are estimated at $0.0065/kWh.

Task 94-2. Complete Development of 17-Ton Single-Effect Air-cooled Absorption Chiller and Integrate with 85 kW Cogenerator ($450K)

The single-effect absorption chiller will have a coefficient of performance (COP) of ~0.7 and a capital cost of $360 per ton. The chiller will utilize cogenerated heat that otherwise would largely be wasted during the cooling season. Absorption chillers do not use CFC's and can be used to replace electric-powered CFC-based chillers. It will be an air-cooled design that will eliminate the need for an expensive cooling tower. The size of the machine is keyed to the reject heat stream from the cogenerator developed in Task 94-1. This will permit direct mating of the chiller and cogenerator at the building site and the cogenerator to be located remotely, with thermal transport between the two via the central steam or hot-water distribution system.

Task 94-3. Develop and Test New Methods of Dual-Fueled Diesel Emissions Mitigation ($250K)

The primary issues to be dealt with on diesel emissions are particulates (soot) and oxides of nitrogen (NOx). Of the two, particulates are expected to work well, but some applications work is needed. The mitigation of NOx will be the primary thrust of this project. The first step will be to estimate the lowest level of achievable emissions using current state-of-the-art techniques including both in-cylinder approaches (water spray, combustion modification) and tailpipe cleanup options [selective catalytic reduction (SCR), selective non-catalytic reduction (SNR)]. In SNR, ammonia is injected into the exhaust stream to promote conversion of the nitrogen oxides to nitrogen and water. SNR is promising when combined with a condensing economizer, which could aid in the recovery of excess ammonia ("ammonia slip") as well as aiding in soot reduction and energy recovery. All these processes are expected to work most effectively if employed within relatively unvarying conditions; hence, designing for a constant-load machine. This enhances the value of coupling the cogenerator thermally to a multi-building distribution system. The approach will be applications-oriented; that is, techniques proven in other combustion applications will be applied to the diesel emissions problem.

FY 1995

Task 95-1. Demonstrate 85 kW Cogeneration Package and 17-Ton Single-Effect Air-Cooled Absorption Chiller ($200K)

The two main items of development from FY94 will be mated and installed at a demonstration site on a selected U.S. Navy base. The system will be monitored for a period of one year. Discussions have been held with responsible personnel at the Naval Surface Warfare Center (Crane Division), Crane, Indiana; however, other possible sites have also been identified by Navy contacts. This project will monitor the performance of the system over a 1-year period incorporating both a heating season and a cooling season. Criteria for evaluating system performance will include: reliability, emissions levels, and energy efficiency as compared with competing system options.

Task 95-2. Develop and Test High-Temperature-Output Version of 85 kW Cogenerator ($100K)

In order to accommodate advance double-effect absorption chilling, with its higher COP, the thermal takeoff temperature of the cogenerator will need to be increased, from ~240 F for the baseline unit to the range of 270 F - 300 F. This will be accomplished through the use of propylene glycol as a heat transfer fluid, reversal of the flow direction from the traditional upflow design, and use of advanced lubricants.

Task 95-3. Develop and Test 35-Ton, Double-Effect Absorption Chiller and Interface with High-Temperature Cogenerator ($500K)

A new high-efficiency double-effect absorption chiller will be developed to supply buildings served by chilled water systems and district cooling. It will be designed to be driven by heat-supplied from advanced cogeneration systems developed in the first task and further modified to produce the higher temperatures that are required by the two-stage absorption systems. The new system can be expected to attain a COP of 1.34 and cost $450 per ton. The overall COP of a combined cogeneration/absorption system when used for chilling is expected to exceed 3.0, compared with 1.5 (including utility-wide energy losses) for conventional electric-driven chillers.

Task 95-4. Develop and Test New Methods of Dual-Fueled Diesel Emissions Mitigation ($150K)

This is the second year of a two-year effort to bring diesel emissions within acceptable limits for widespread cogeneration applications. Efforts will emphasize integration into the actual cogenerators being developed under parallel projects.

FY 1996

Task 96-1. Demonstrate High-Temperature 85 kW Cogenerator and 35-Ton Double-Effect Absorption Chiller ($250K)

This task will follow the pathway established in Task 95-1, but employing the more-advanced equipment developed during FY95. The higher tonnage of the absorption chiller reflects the larger thermal COP of the unit. Location of the two demonstrations in the same test location will permit direct comparisons with respect to reliability, emissions, and energy efficiency.

Task 96-2. Develop and Test Scaled-Up 750 kW Version of the Higher-Temperature Cogenerator and Double-Effect Absorption Chiller ($700K)

In this task, design and development work will proceed on a nearly ten-fold upsizing of the advanced units developed during the preceding year. It is expected that this scaleup will permit economies of scale and emissions reduction when compared with the smaller units, and will also permit their employment in larger buildings and larger community thermal distribution systems. Design goals are $500/kW installed for the cogenerator and %350 per ton for the double-effect absorption chiller.

FY 1997

Task 97-1. Demonstrate the High Temperature 750 kW Cogenerator and 350-Ton Double-Effect Absorption Chiller on a Naval Base, and Monitor for One Year ($950K)

This task represents the culmination of the four-year effort, in which a technologically mature unit is made available for more widespread application with the Navy, the military generally, and the civilian sector. The continuity of three years of demonstrating ever larger and more sophisticated units will provide a high degree of credibility with military and civilian-sector decision makers.

8. Expected Payoff:

This proposal addresses the existing situation of military-base district heating systems and general supply, which is in need of significant economical upgrades in energy efficiency. As a result of exiting conditions and future prospects, there has been much discussion of abandoning the bulk of these district heating systems and replacing them with individual building heating, ventilating, and cooling (HVAC) systems. However, that would not constitute an optimal solution, since it would not only mean scrapping 6,000 miles of pipeline worth $12 billion, but replacing it with individual-building HVAC systems that in the long run could prove to be just as problematic from the standpoint of economy, energy efficiency, and environmental quality.

If the goal of this project is met, a new generation of advanced cogeneration and absorption chilling technologies will provide specific benefits to the military services including:

- Fuel savings up to 50% compare with conventional systems
- Drastic reductions in local and global air pollution
- Elimination of CFC refrigerants from HVAC equipment
- More reliable sources of electric power, space heating, and space cooling supply

- Significantly reducing electricity costs, especially those relating to electricity and air-conditioning energy supply

9. Milestones:

1.	Complete Development and Test of Advance 85 kW Cogeneration Packaged System and 17-Ton Chiller	3/95
2.	Complete Diesel Emissions Mitigation Development	3/96
3.	Demonstrate Packaged Cogenerator and 17-Ton Chiller	3/96
4.	Complete Development and Test of High-Temperature Cogeneration and Double-Effect	3/96
5.	Demonstrate High-Temperature Cogenerator/Chiller	3/97
6.	Complete Scaled-Up Cogeneration System Development	3/97
7.	Demonstrate Scaled-Up System	3/98

10. Transition Plan:

Technology transfer will be promoted through the demonstration projects scheduled for this and succeeding years, which will be designed with the military and civilian sectors clearly in mind, and by industry interaction, user-community involvement, and general publications in technical and industry oriented periodicals. BNL's Technology Transfer Office will assist in the formation of CRADAs when feasible.

11. Funding: ($K)

FY94	FY95	FY96	FY97	TOTAL
300	950	950	950	2,200

12. Performers:

Work will be performed by Brookhaven National Laboratory. We anticipate that Modular Cogeneration Corporation, Mt. Vernon, New York, will be a key industry partner along with other industry partners identified in the course of the work.

13. Principal Investigator:

Dr. John W. Andrews
Brookhaven National Laboratory
Building 526
Upton, NY 11973
TEL: 516 282-7726
FAX: 516 282-2359

14. Keywords:

Cogeneration, absorption, district heating, diesel engine, energy efficiency

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Energy Conservation/Renewable Resources

2. Title: Optimize Energy Efficiency AC Induction Motor

3. Agency: Environmental Protection Agency (EPA)

4. Laboratory: Air and Energy Environmental Research Laboratory (AEERL)

5. Proposal ID: #231

6. Problem Statement:

Goal: Electric motors use 2/3 of the electrical energy produced in the US. Military electrical use is comparable. Use is dominated by large AC induction motors (5 to 10,000 hp) used for HVAC, water distribution, steam plant draft fans and boiler pumps, and lifts and conveyors.

Motors alone are relatively efficient devices, converting 65% to 95% of their electrical supply to useful mechanical energy. However, constant speed motors used for such common applications as driving large pumps or fans, flow is often regulated by valves or dampers. This results in a waste of motor output power.

The best solution to this problem is the power electronics device called the adjustable speed drive (ASD), which varies the line voltage and frequency to a motor, allowing it to operate at different speeds. However, ASDs usually do not control motors at their most efficient operating condition.

Background: The program goal is to increase the efficiency of AC induction motors on US military installations. The proposed solution applies new, low-cost, laboratory-tested motor control techniques, to reduce military installation energy consumption by up to 8%. The reduction in energy use will aid DoD to reduce emissions (greenhouse and acid rain gases) because of the avoided electrical power plant fuel consumption. This will enable the DoD to comply with environmental regulations and maintain energy security.

Existing Effort: To gain additional efficiency improvement, AEERL/EPA is currently sponsoring work on a new efficiency optimizing controller to complement ASDs. The problem of minimizing motor power input has been addressed and essentially solved at the motor control simulation and testing facilities of the Research Triangle Institute (RTI) in Research Triangle Park, NC. Controllers have been designed, simulated, and tested in the laboratory with excellent results. However, field demonstration and final design optimization remain to be accomplished. The new controller set minimizes motor power use in 3 ways:

1) Optimizes the ASD functions to set motor control at the most efficient energy point on any motor's operating curve;
2) Corrects the inherent error between frequency setting and motor rotational speed setting;
3) Adapts to any motor's operating environment, so that available process sensors and feedback are used to advantage.

An innovative approach being used is fuzzy logic. Widely applied in Japanese products, this mathematical technique improves control for non-linear problems such as motor control.

Control is accomplished by a voltage perturbation scheme and a unique motor speed predictor-corrector that eliminates the need for speed encoders or tachometers. This is important because speed measuring devices can double motor costs and increase maintenance, calibration and failure problems. Only one additional motor measurement is needed to minimize line power while maintaining rotary speed within 0.2%. The controller is passive and needs no additional setting or calibrating after initial parameters are programmed.

Typical laboratory results obtained with five and ten horsepower motors have demonstrated input power reductions of from 1% to 15%, while using a high-efficiency ASD. For pump/fan applications where no ASD is being utilized, the addition of the controller set with an ASD could save over 30 to 40% of the energy being consumed by the constant speed motor.

7. Project Description:

Technical Objective: The first objective is to demonstrate the ability of the EPA/RTI control scheme to produce significant reductions in the energy required by continually operating applications. Also, any existing controls already in place will be integrated into efficiency optimization in a cost effective manner. The project will demonstrate that technical barriers can be overcome and that the payback period for the investment in efficiency is well below guidelines. An additional objective is the transfer of this technology to the private sector. A new ASD/controller combination which would always run a motor at the peak efficiency possible should be another result of the effort.

Technical Approach: Suitable application sites will be chosen in consultation with the Facilities Engineer at the installation. For example, the following list of potential application sites was chosen in consultation with Utilities and Facilities & Maintenance personnel at the 18th Airborne Corps. and Ft. Bragg in Fayetteville, N.C. Ft. Bragg, a U.S. Army installation with a population of over 61,000 people, consumes electrical energy at a rate of 43 megawatts (about 60,000 hp). Similar applications exist at the Cherry Point, N.C. Naval Air Station, Seymour-Johnson Air Force Base in Goldsboro, N.C., and at military installations across the country. Some Ft. Bragg testing options are:

1) Induced draft fans for boiler combustion air, typically 100-125 hp fan motors which use dampers, like many military base steam generation facilities. Cherry Point NAS engineers are also very interested in retrofitting boiler fan motors.
2) Hot water distribution pumps, e.g., a 100 hp pump motor with line pressure regulated using an expansion tank, with all water pumped to the tank representing net waste of energy.
3) Chilled water distribution pumps, such as a 125 hp motor with supply regulation by bypass valves which return excess flow to the chiller. The pump motor runs at 100% capacity.

The largest motors at Ft. Bragg are in the 600 to 3500 hp range. A power monitor will be installed at each test site to gather baseline data on the power consumed by the motor. The period of monitoring will be either sufficiently long to smooth out seasonal effects and other natural perturbations, or the data will be adjusted in accordance with past utility records. While the baseline data is being obtained, the application sites will be evaluated to see if improvements

can be made in the control of the process which will make the process more efficient. Throttling devices and other inefficient controls will be disabled.

The application sites will then be modified to allow for the demonstration of the technology. If the sites do not currently have ASDs, these will be installed. This device will be obtained from a U.S. manufacturer who will assist the project team in installation and in interfacing the ASD to control and monitoring systems. If the application sites employ ASDs, the units will be evaluated to see whether they can be retrofitted with the controller, or if other ASDs should be substituted.

The applications will be run with the new control system, and the input power consumed by the motor monitored for a period corresponding to the baseline data. Then, the power consumed will be compared to the baseline data. Other recorded data will include speed, output power, voltage, frequency and current levels. Maintenance records, any anomalies, (e.g., over-current conditions), and motor stator temperature will also be maintained.

Coordination between military, research, and industry representatives will be required. Each task will have a team which will coordinate on that task. The base Facilities Engineer or the base Energy Conservation officer is anticipated to act as liaison between the research personnel and the base personnel.

Innovative Aspects: The controllers to be demonstrated and optimized are unique inventions, and there is no indication that their level of performance has been equalled elsewhere. The modification of the control algorithms of an ASD in order to produce the most efficient operating point possible for a motor has been demonstrated in the laboratory, but not field-tested. This project would provide a unique proof of application of this technology.

Single chip embedding of the controller set with conventional ASD circuitry would be a pioneering result of this research. The concept of process control for energy efficiency has been discussed by the private sector. This project would provide an opportunity to include this profitable concept in facility design and maintenance. The associated concept of design for energy efficiency, widely adopted by the private sector, would be a natural extension of this process.

Tasks:

1) Review all potential applications or combinations of applications at the military base. Test applications will be selected based on the size of their energy impact, and be representative of military installation applications in general. The sites selected will allow a high probability of success within the constraints of the budget, and should address user needs. A computer simulation of the test sites will predict the controller performance.
2) Install power meters and other instrumentation measuring current, voltage, temperature, frequency, etc. at each site and initiate baseline monitoring. Install a computer and other suitable monitoring equipment at each site, in a protected environment.
3) Make any obvious improvements to the existing process control to improve efficiency and repeat baseline monitoring.
4) Install the new controller sets (and ASDs if necessary) and start up and shake down. Add instrumentation to the ASD as required, including the establishment of communications links.

5) Initiate the demonstration, and take short term (e.g., 24 hour) data sets. Modify operating conditions within the requirements of the installation and repeat testing for several conditions. Analyze demonstration results.
6) Perform long-term (weeks to months) tests, emphasizing power consumption integrated over the test period and compared with long-term baseline data.
7) Transfer technology to private sector industry. This task will be initiated at the beginning of the project and continued throughout. A manufacturer of the high-efficiency controller will be enlisted. Final assessments of demonstration results will determine decisions on markets, costs, and further development requirements.

8. Expected Payoff:

Program results will provide an important and low-cost step toward reducing energy use by 20% by 2005, to return CO_2 to 1990 levels, and eliminate up to 8% of SO_2 from plants supplying electricity to military installations. Based on results obtained with the new motor controller, and on the annual electrical budget for the Department of Defense (DoD), application of the controller alone could save 2 billion kilowatt hours and $130M in annual energy costs at military installations. Major environmental results are preventing the emission of 2 million tons of CO_2 and 80,000 tons of SO_2 each year into the atmosphere. The controller is also more accurate for motor speed control.

The payback time (based on energy savings alone) for a new efficiency controller ($25 chip set) added to a 20 hp motor/ASD is estimated at 60 days, and for a 200 hp motor only 6 days.

Finally, the provisions for technology transfer in the project open motor control market opportunities exceeding $10 million.

9. Milestones:

1.	Select motor applications and motor drive(s)	06/94
2.	Complete baseline data monitoring	11/94
3.	Complete installation of controllers, startup, and shakedown	01/95
4.	Complete short term testing	07/95
5.	Complete long term testing with and without controller	05/96
6.	Complete final multi-facility assessment and commercial transition	09/96

10. Transition Plan:

Transfer technology potential is high. The goal of energy efficient electric motors and processes is as important commerically as militarily. Because only a few commercial motors use ASDs, pollution and energy savings potential in the commercial sector is even larger than that of the military sector. Therefore, industry representatives interested in the development and incorporation into an ASD will be sought as licensees of the technology. Cost-sharing of development of the ASIC will be given priority, with funding mechanisms and agreements which minimize the time between product development and market appearance. U.S. manufacturers have already expressed an interest in the efficiency optimization process and the controllers described above.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	250	350	350	950
EPA	160	230	120	510
MILITARY INSTALLATION*	25	25	25	75
RTI	25	25	25	75
TOTAL	460	630	520	1610

* Labor and facilities in-kind.

12. Performers:

Technology demonstration will be performed through the cooperation of EPA (AEERL), DoD (via selected military installation), RTI, an ASD/motor vendor (e.g., General Electric, Westinghouse, etc.), and possibly a power semiconductor developer/vendor (Harris Semiconductor). An EPA cooperative agreement exists for partial funding. The DoD contract is Mr. Michel Laurencense, Director of Public Works and Environment, Ft. Bragg, Fayetteville, NC.

13. Principal Investigator:

Dr. Ronald Spiegel (MD-63)
USEPA
Research Triangle Park, NC 27711
Phone: (919) 541-7542
FAX: (919) 541-2382

14. Keywords:

Motor control; adjustable speed drive; fuzzy logic; slip optimization; induction motor; power electronics

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Fuel Cells for Military Applications

3. **Agency:** Army

4. **Laboratory:** US Army Construction Engineering Research Laboratories

5. **Proposal ID:** #641

6. **Problem Statement:**

The majority of central heat plants on U.S. military bases are nearing the end of their useful life and will soon need replacing. This presents an opportunity to replace existing equipment, based on energy concepts developed almost eighty years ago, with current state-of-the-art or near-term emerging technologies. Fuel cells are electrochemical power generators with the potential for attaining very high electrical energy conversion efficiencies while operating quietly with minimal polluting emissions. In addition, by-product thermal energy generated in the fuel cell is available for use for cogeneration of hot water or steam, bringing the overall potential conversion efficiency (electrical plus thermal) to the order of 80%. The extremely low environmental impact associated with fuel cell technology is in direct support of DoD/DOE environmental objectives. Air emissions for key pollutants (SO_2, NO_x, and particulates) range from negligible (orders of magnitude below New Source Performance Standards [NSPS] of the Clean Air Act for SO_2) to undetectable (for NO_x and particulates) with gas or distillate fuels. Superior environmental performance also can be achieved using coal gas as a fuel. Because of the high energy conversion efficiency, fuel cell power plants also produce lower levels of greenhouse effect pollutants (such as carbon dioxide). Phosphoric Acid Fuel Cells (PAFC) are currently entering the initial stages of commercialization. Molten Carbonate (MCFC) and Solid Oxide (SOFC) fuel cells, offering even higher electrical energy conversion efficiencies and increased cogeneration utility, are expected to become commercially available around the turn of the century. This project is a continuation of an ongoing SERDP program designed to provide a field demonstration of PAFC technology at U.S. military installations, with the resultant lessons learned to be applied to the development of application guidance for the eventual implementation of MCFC and SOFC technologies within the DoD.

7. **Project Description:**

The technical objective of this project is a demonstration of the applicability of fuel cell technology to U.S. military installations. This involves the development of application guidance for PAFC technology, screening of U.S. military installation pertinent data against this application guidance, development of an implementation plan for PAFC installation within DoD, monitoring of the resultant purchase and installation procedures, monitoring of system performance, documentation of lessons learned, and application of lessons learned to provide guidance for similar implementation plans for use with MCFC and SOFC technologies as they become commercially available.

This project is related to current and outyear COE sponsored R & D work units concerned with advanced electrical supply strategy and the assessment of emerging fuel cell technology for

eventual DoD application. It is also related to a DoD funded effort to provide application guidance for PAFC technology within the DoD. In addition, the 1993 Appropriation Act provides for $18 million ($6 million each for Army, Navy and Air Force) procurement accounts for non-developmental item natural gas fuel cells currently in production in the U.S. for power generation at military installations, with recommendation for locations in need of enhanced air quality. This funding can be used for system design, purchase of fuel cells and balance of system, and system installation. SERDP funding is primarily requested for the development of the PAFC implementation plan for DoD and for monitoring the resultant acquisitional, installation, and operational aspects involved with fuel cells.

Primary technical risks involved in this project are concerned with the current costs of fuel cell systems. At the present time, fuel cells are not economically competitive with other more conventional energy production technologies. Their primary application must therefore be based on environmental considerations. Current cost projections predict that PAFC systems will become economically competitive within the next 3 - 4 years as market demand increases. This will have to occur before fuel cell technology can be considered as an energy supply alternative based on energy conversion efficiency considerations alone.

Progress on this project to date includes the coordination of the efforts involved in this project with other U. S. Government sponsored fuel cell efforts. Efforts are currently underway to publicize progress and results of this project through established DOE communication pathways. The experience of EPA laboratories (AEERL) in quantifying environmental benefits resulting from the application of fuel cell technology will be used in the assessment of the results of this project. USACERL has also been named as the DoD Technical Stakeholder for a related project being conducted by the National Defense Center for Environmental Excellence (NDCEE) involving a 400 kW air-cooled PAFC. USACERL and representatives from the Tri-Services, acting under the oversight of the Defense Utility Energy Coordinating Council (DUECC), has coordinated efforts to establish a list of potential candidate sites for PAFC demonstrations. Initial PAFC application guidance has been established and pertinent data from the candidate sites is currently being screened against this guidance. A solicitation for the purchase of turnkey PAFC fuel cell systems has been prepared. Responses to this solicitation are currently being evaluated and contract award is expected to proceed shortly.

8. Expected Payoff:

Initial applicability will probably be restricted to DoD installations located in air quality non-attainment regions. The benefit in these cases will be an acceptable level of progress made toward attainment, and reduction or elimination of fines resulting from violations. As production costs decrease, fuel cell technology should prove to be cost-effective based on electrical energy production costs alone. Current industrial projections predict mature market installed costs for PAFCs to be less than $2000/kW. With expected natural gas prices at $4.00/MBtu, these systems should be cost effective in any region in which electric energy costs exceed 5.5 cents/kWh, provided a need for the thermal energy produced exists.

9. Milestones:

1.	Develop PAFC application guidance for DoD	12/93
2.	Collect pertinent DoD energy consumption/cost data	12/93
3.	Collect pertinent DoD environmental compliance data	12/93
4.	Determine Utility Company leveraging opportunities	04/94

5. Develop PAFC implementation plan for DoD 07/94
6. Develop RFP for delivery of turnkey PAFC systems 09/94
7. Develop PAFC performance test plan 12/94
8. Complete PAFC purchase/installation process 09/95
9. Complete PAFC system performance monitoring 09/97
10. Document PAFC program lessons learned 09/98

10. Transition Plan:

Discussions held with industry representatives indicate that current production capabilities of one commercially available 200 kW PAFC is approximately 5 units per month. This fits easily into the projected project time frame. Increased market demand should be accompanied with increased production capability such as to meet any potential future DoD requirements. Development of the implementation plan and the subsequent monitoring of implementation and operational activities should serve to assure that user requirements are given full consideration. Lessons learned from this project will be incorporated into separately OCE-funded R & D efforts to assess the potential applicability of MCFC and SOFC technologies to DoD facilities.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	350	350	300	250	150	0	1400

12. Performers:

The extensive experience of DOE laboratories and private research organizations (e.g. EPRI, GRI) in fuel cell technology applications will be incorporated. DoD contractors who have demonstrated expertise in the fuel cell technology arena will be employed during the program. The experience of EPA laboratories in quantifying environmental benefits resulting from the application of fuel cell technology will be employed. Selection of the candidate PAFC demonstration sites as part of the implementation plan will be coordinated among the Tri Services. Potential leveraging opportunities available as part of existing or negotiable incentive plans offered by local gas and electric utility companies will be identified and incorporated into the project where applicable. Overall project oversight will be provided by the Defense Utility Energy Coordinating Council (DUECC).

13. Principal Investigator:

Mike Binder
U.S. Army Construction Engineering Research Laboratories
ATTN: CECER-FEP
P.O. Box 9005
Champaign, IL 61826-9005
(217) 398-5509 (Commercial)
(217) 373-3740 (Fax)

14. Keywords:

Fuel cell, Electric power, Natural gas, Cogeneration, Alternate energy, Emissions

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Advanced Cycle Mobile Heat Pump

3. Agency: Air Force

4. **Laboratory:** Wright Lab

5. **Proposal ID:** #094

6. Problem Statement:

Global goals have been established to reduce and eliminate the use of CFC's due to the global warming issue. Federal regulations require that certain CFC's be phased out by 1995. To accomplish this, new cooling technologies must be explored. New energy-efficient field-deployable Environmental Control Units (ECU) can be developed to replace current units. By utilizing new technology in the thermodynamics field, new heat-pump cycles can be applied that allow cooling without using the ozone-depleting CFC's that normally occur in the cooling cycle.

7. Project Description:

This is a continuation of an FY93 funded SERDP project to assess the feasibility of using advanced heat pump cycles (Stirling, Vuillemier, etc) to provide a bare base with highly efficient, low maintenance heating, ventilating and air conditioning (HVAC) systems. Various design concepts for heat pumps will be examined such as direct- absorption-vapor compression cycles, acoustic air conditioners and compressorless refrigeration cycle technologies. An analytical model for the selected concept will then be developed. This model will be used to engineer the new heat pump to meet bare base requirements. The resulting configuration will be analytically tested and its performance data compared with the current system to determine cost effectiveness of the new equipment. This effort will eliminate the use of CFC's on deployable heat pumps and provide a more energy efficient method of generating cooling. This will reduce the amount of fuel needed to meet HVAC requirements.

8. Expected Payoff:

The successful completion of this project will produce the technology for a new generation of heat pumps that will not use ozone depleting CFC's and will require less energy.

9. Milestones:

1.	Start Program	09/93
2.	Literature/Technology Review	12/93
3.	Thermodynamic Cycle Analysis	02/94
4.	Energy/Economic Feasibility Analysis	05/94
5.	Small Scale Testing	09/95

10. Transition Plan:

The results of this R&D will be transferred to the Air Force for full scale application. The technical report and professional publications will be distributed to the Air Force MAJCOMs, DoD, DoE and the research and development community.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	500	850	650	2000

12. Performers:

Wright Laboratory, Flight Dynamics Air Base System branch will perform a portion of this work in-house. Some thermodynamic research is to be conducted by Nevada Engineering Research and Development Systems.

13. Principal Investigator:

Douglas E. Klaymeier
WL/FIVCO-OL
139 Barnes Drive Suite 2
Tyndall AFB, FL 32403-5323
TEL: (904) 283-3730
FAX: (904) 283-3722
DSN 523-3730 DSN-Fax 523-3722

14. Keywords:

Heat Pump, Thermodynamics, ChloroFluoroCarbon (CFC), Refrigeration

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Energy Conservation/Renewable Resources

2. Title: Thermal Acoustic Piezoelectric Power Generator

3. Agency: Defense Nuclear Agency

4. Laboratory: NA

5. Proposal ID: #084

6. Problem Statement:

Heat is universally abundant either as a natural resource or as the by-product of a process. Depending on the specific environment, waste heat is naturally transferred through convection or conducted through a cooling process. A number of methods are available to transform heat into electrical power. These include thermoelectric and thermionic. The problem with existing approaches is that the efficiency is too low and/or the cost too high to provide a marketable product.

7. Project Description:

The proposed project develops a 5 to 10 kW, AC power, Advanced Technology Demonstrator (ATD) using thermal sources, a natural heat engine developed by Los Alamos National Lab and a highly efficient piezoelectric transducer developed by Ballistic Missile Defense Organization (BMDO) for space power applications. Overall efficiencies of 30% to 40% and system power/mass ratio between 0.8 to 1.0 kW/kg are predicted.

TASKS

1) The heat engine efficiency will be optimized. Tubular and radial configurations will be evaluated. High temperature materials and working fluids will be investigated.
2) The frequency of the heat engine will be optimized. The initial design point will be a nominal 400 hz, however, higher frequencies, in combination with frequency converters, will be investigated.
3) Piezoelectric transducers will be scaled up in size. Series/parallel connection options will be evaluated for tubular compression stacks and radial configurations.
4) A 5 to 10 kW ATD will be fabricated and tested.

8. Expected Payoff:

It is expected that the final product of the effort will be capable of generating power at 50% of the cost compared to conventional methods. Not only will the efficiency be doubled, but also the approach requires no field excitation, bearings or other items necessitated by rotating machinery.

The cost to benefit ratio for this project is maximized by building on work previously funded by BMDO and previously developed by LANL. Other agencies, including NASA, USAF, USA

and the State of Texas have expressed interest in applications for TAP. Discussions with appropriate offices within these organizations are ongoing.

9. Milestones:

1. Test tubular heat engine	FY94
2. Design, fabricate, test radial engine. Scaleup piezoelectric stack.	FY95
3. Fabricate and test 5 to 10 kW generator	FY96

10. Transition Plan:

Upon completion of the development of the Thermal Acoustic Piezoelectric Power Generator (TAP), the contractor will license the power generator to industry.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	Total
BMDO	80K	0	0	0	80
SERDP	0	100K	125K	150K	375

12. Performers:

DNA managed. University of Texas, Arlington, Texas prime contractor. Dr. W. E. Dillon

13. Principal Investigator:

Mr. Andy Fahey
Defense Nuclear Agency/RAST
6801 Telegraph Road
Alexandria, VA 22310-3398
TEL: 703 325-7087
FAX: 703 325-2959

14. Keywords:

Piezoelectric, Electrical Power, Heat Engine

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Geothermal Space Conditioning for Large DoD Buildings

3. **Agency:** Department of Energy

4. **Laboratory:** Sandia National Laboratories

5. **Proposal ID:** #580

6. **Problem Statement:**

Electricity production for space conditioning (heating and cooling) and water heating at DoD facilities generates an estimated 18 million tons of CO_2, 68 tons of SOx, and 30 tons of NOx annually. In addition, significant amounts of environmentally harmful refrigerants are released to the environment from DoD space conditioning systems. DoD electricity costs alone for heating, cooling and water heating of facilities is estimated to exceed $700 million annually. The total space conditioning cost to DoD is amplified by major operation and maintenance expenses.

The use of geothermal heating, cooling, and water heating systems - hereafter referred to as "geothermal space conditioning" systems (which include geothermal heat pumps, ground water cooled chillers, heating with geothermal direct use, and water systems used as heat sources and sinks) - has the potential to save 20-50% of the energy and emissions when compared to conventional technologies. For example, geothermal heat pumps (GHPs) use about 30% less electricity compared to air-source heat pumps and 50% less than electric resistance heating. The EPA study (Space Conditioning: The Next Frontier, April 1993) on residential space conditioning and water heating options and notes that geothermal heat pumps have the lowest overall environmental cost and the lowest lifecycle costs of available technologies. GHPs also have the lowest CO_2 emissions of HVAC equipment, reduce refrigerant use up to 75%, reduce utility demand charges for peak loads, and lower maintenance costs substantially.

The use of geothermal space conditioning systems will also assist DoD in switching to ozone friendly refrigerants, a key challenge at large buildings. According to the Heating, Piping, & Air-conditioning Journal (April 1993), it is estimated that "some 22,000 low-pressure chillers must be retired from 1996-1998 if chiller owners are to have enough reclaimed CFCs to maintain the remaining installed base of equipment." In addition, the GSA is expected to spend about $100 million annually over the next 3-5 years to address the CFC issue. The successful implementation of this program will assist DoD in achieving a 20% reduction in energy consumption by the year 2000 as required in Executive Order 12759, and meeting the goal of the National Defense Authorization Act for FY91 which calls for DoD to install 100 MW of renewable technologies.

Major barriers to the accelerated and expanded use of geothermal space conditioning and water heating systems are: 1) lack of awareness about the technologies; 2) availability of data on costs and performance in a DoD context; 3) shortage of sufficiently trained DoD personnel to design, specify, operate and maintain these systems; 4) difficulties in specifying and procuring these systems through the existing DoD procurement process; and 5) higher first - but typically the lowest lifecycle - costs.

7. Project Description:

The initial SERDP funding in FY93 is focused on introducing and rapidly expanding the use of geothermal heat pumps in base housing and small DoD buildings. The DoD Oversight committee on the SERDP Geothermal Space Conditioning Program (which includes representatives of each service, the Defense Energy Policy Office, DoD research organizations, and DOE and EPA) has articulated the overall goal of this program as:

> Developing a permanent DoD capability to evaluate, design, install, operate, and maintain geothermal heat pumps to reduce maintenance costs, environmental impacts, and electric power consumption for space heating, cooling, and water heating, saving DoD an estimated $50 to $100 million annually by the year 2000.

A Multi-year Work Plan defines program objectives and milestones.

The new FY94-8 proposal will expand the GHP program to target the heating and cooling needs of large DoD buildings (over 50 tons), which constitute the majority of building square footage at DoD facilities. A parallel R&D and performance contracting program aimed at overcoming the higher first cost will b pursued as appropriate. The major objective of the FY94-98 program will be to establish a permanent DoD capability to specify, design, procure, operate and maintain GHP systems and ground water cooled chillers at large buildings. These technologies will be demonstrated and evaluated at DoD facilities within the next three years, and technology transfer completed with widespread DoD acceptance within five years.

Geothermal space conditioning and water heating systems at large buildings will be designed and demonstrated to eliminate the need for cooling towers (a major DoD maintenance consideration requiring skilled personnel and use of chemicals), eliminate the need to shift to more energy intensive air-cooled towers, and reduce the use of ozone damaging CFCs.

The primary technical challenge to ground water cooled chillers will be to determine the co-location of adequate ground water sources with DoD facilities. Water use may be restricted by local regulations, be required to inject most or all the water, or be to warm in a few instances for cost effective cooling.

The critical path to success for this five-year program consists of identifying the best use of these technologies at DoD facilities nationwide, installing, operating and monitoring demonstration projects, documenting the results on a regional basis to factor in climate and geologic variations, developing design criteria and software, and educating and encouraging DoD decision-makers to adopting these geothermal technologies on a widespread scale.

R&D will be performed only if analyses show potential to reduce costs at least 15% within three years. If such R&D needs are not identified, funds will be shifted to field demonstrations at additional sites. DOE, in conjunction with the Electric Power research Institute, National Rural Electric Cooperative Association and others, is currently researching lower-cost ground coupling systems ranging from advance drilled bits or components, to thermally enhanced grouts for wellbores, to granulated backfills for slinkys, to optimizing loop lengths.

8. Expected Payoff:

Successful completion of the overall Geothermal Space Conditioning Program (FY93-FY98) will result in: 1) emission reductions at the power plant of approximately 3.6 million tons of CO_2, 13.6 tons of SOx, and 6 tons of NOx; 2) a 10% reduction in electricity used in heating, cooling and water heating, saving $50 to $100 million annually from the use of geothermal space conditioning and water heating in residential and small DoD buildings; 3) another 10% savings in energy and emissions from the use of geothermal space conditioning and water heating at larger DoD buildings (new FY94-98 program), saving another $50 to $100 million annually; 4) reduced refrigerant use by up to 50% for the small building portion and a significant amount for large buildings (at present undetermined due to the wide range of existing equipment); 5) at least a 10% peak electric demand reduction for DoD facilities; 6) significant but unquantified maintenance savings; and 7) opportunity to "fast track" an energy and environmentally beneficial renewable energy technology for Federal Government-wide application.

Base on an extremely conservative annual energy savings of $50 million for DoD, the benefit-cost ratio for this program would be in excess of 500:1 over ten years. In addition, environmental and cost savings would accrue from reduced power plant emissions and refrigerant releases, reduced maintenance and downtime costs, and improved reliability.

9. Milestones:

1.	Select 1-2 new GHP demonstration sites	9/94
2.	A&E guidance on working/designing GHPs for DoD facilities	10/94
3.	Develop performance contract/procurement process guidance	12/94
4.	Select first 1-2 ground coupled chiller sites	12/94
5.	Develop protocols for collecting/analyzing chiller data	10/94
6.	Install ground coupled chiller systems	4/95
7.	Sponsor DoD teleconference on technology/case studies	10/95
8.	Develop GHP modules for design software/manuals	12/95
9.	Select 1-2 new geothermally-based systems	12/95
10.	Design and install new systems	10/96
11.	Update data analysis of systems installed over 1 year	10/96
12.	Select & design 1-2 new geothermally-based systems	10/96
13.	Develop ground coupled chiller design manual/software	6/97
14.	Analyze electric load data & CFC benefits for chillers	8/97
15.	Seminars/workshops on DoD case studies	1/98
16.	Seminars/workshops for A&E firms & utilities, etc.	9/98
17.	Provide technology transfer, design assistance	94-98

10. Transition Plan:

Transitioning of the geothermal space conditioning and water heater technology from the demonstration stage to end-user and commercial applications is a major and integral aspect of the proposed effort. The program transition plan targets to distinct audiences: 1) potential DoD decision-makers and end-users of geothermal space conditioning technologies and associated services.

Involvement of key DoD decision-makers and end-user organizations in the entire program planning and execution phases is a fundamental transition strategy. Primary partners in this

program are the DOE Geothermal Division - lead organization charged with technology development and demonstration and the U.S. Army Construction Engineering Research Laboratory (CERL) - one of the lead DoD organizations charged with evaluation and information dissemination of HVAC technologies. In addition, involvement of the U.S. Army Cold Region Research and Engineering Laboratory (CRREL), U.S. Navy Engineering Facilities Command (NAVFAC) and the Naval Facilities Engineering Services Center (NFESC), Ft. Polk, and the Patuxent River Naval Air Station in the planning and demonstration stages has already been arranged. This program also has an ongoing working tasks with working task with the DOE Federal Energy Management Program (FEMP), and the Federal Energy Technology Test Bed Program managed by the Pacific Northwest Laboratories. Tasks on data collection and analysis, technology evaluation, education and awareness, technical training, and procurement process facilitation constitute a major part of the proposed effort. This strategy will ensure that the technology, information, and know-how will be effectively transferred to DoD (and other federal agencies). Appropriate DoD-oriented technology software and modules for design and procurement manuals will also be developed.

Transitioning to the private sector infrastructure will be accomplished by both specific program tasks as well as by early and continuous involvement and consultation with equipment manufacturers, utilities, A&E firms, HVAC installers and servicers, and industry trade groups. These parties will be explicitly involved through participation in cost-sharing demonstration projects, design and installation contracts, and DoD-oriented workshops/seminars/teleconferences, etc. A number of these organizations have already expressed interest in working with DOE and DoD to demonstrate and promote geothermal space conditioning technologies.

11. Funding: ($K)

The SERDP Geothermal Space Conditioning Technology for Large DoD Buildings Program will be implemented in concert with the ongoing DOE Geothermal Heat Pump Program. While the objectives and tasks of the two will be implemented separately, the DOE program will support and enhance the SERDP effort.

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	800	800	1,200	1,200	1200	5,200
DOE	100	200	200	200	200	900
UTILITY*	300	500	500	1,000	1,000	3,300

* Combination of trade association monitoring assistance, utility rebates, incentives, and design assistance.

12. Performers:

CERL - program partner, Ft. Hood demonstration/evaluation lead, design software development
Sandia National Laboratories - technical/administrative management
Pacific Northwest Laboratories - Test Bed Program
Oklahoma State University - GHP technical assistance
CRREL - management of data collection and technology demonstration (initially at Ft. Polk)
NACFAC/NFESC - data collection and technology demonstration at Naval facilities
Oregon Institute of Technology - design assistance on geothermally-cooled chillers
National Ground Water Association - assistance on water well programs

Trane, Climate Master, Water Furnace, Carrier, etc. - equipment suppliers, technical assistance
A&E firms, installers, utilities, industry trade group, etc.

13. Principal Investigator:

Lew W. Pratsch
Department of Energy
1000 Independence Avenue
Washington, D.C. 20585
TEL: (202) 586-1512
FAX: (202) 586-5124

14. Keywords:

Geothermal, heat pumps, ground source, chillers, emissions, renewable energy

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Clean Liquid Fuel from Biomass and Carbonaceous Wastes

3. **Agency:** U.S. Environmental Protection Agency (EPA)

4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)

5. **Proposal ID:** #210

6. **Problem Statement:**

In accordance with the goals of the Energy Policy Act of 1992 and the National Energy Strategy of 1991/92, this project is aimed at the development of a technology that will minimize the cost of producing a liquid alternative fuel and maximize petroleum displacement while achieving greatest reduction of greenhouse gas emissions from mobile sources. Analyses carried out at this laboratory show that the most practical strategy for achieving those goals is to displace petroleum fuels with methanol derived from renewable biomass supplemented with natural gas as cofeedstock. In the long term, development of methanol as a primary alternative fuel will facilitate the transition to fuel-cell powered vehicles that will ultimately replace internal combustion engines and greatly increase fuel economy while eliminating the toxic emissions responsible for noncompliance with environmental standards in major U.S. cities.

Among the renewables, biomass is the only energy resource that can displace petroleum by conversion to a liquid fuel. Although the most practical strategy for minimizing greenhouse gas emissions from mobile sources--which account for 30% of the U.S. total--is to displace gasoline with a liquid fuel derived from biomass, the amount of biomass that could be produced sustainably on a scale large enough to impact the needs of the transportation sector is estimated by Oak Ridge National Laboratory to be only 3-6 quads. Since a 30% displacement of transportation fuel would require nearly 7.5 quads in the year 2010, and because about half of the biomass energy is lost when converted to liquid fuels by existing technologies, the biomass must be supplemented with an additional feedstock that is compatible with the chosen alternative fuel. The efficiency of energy conversion, from biomass to liquid fuel, and a capability to leverage the biomass with a compatible feedstock are crucial to the problem of achieving maximum displacement of petroleum. Process simulations show that the proposed technology can, in theory, leverage biomass with natural gas to produce more liquid fuel from a given biomass supply than any existing process, or combination of processes, while also leveraging the amount of liquid fuel that can be obtained from domestic natural-gas resources and reducing net greenhouse gas emissions.

In the thrust area of Energy Conservation/Renewable Resources, this project will address the following needs defined by SERDP: (1) use of alternative energy sources by substitution of biomass, either from wastes or from energy farms dedicated to large scale conversion to liquid fuel, (2) reduce emissions to comply with regulations by reducing ozone precursors and toxic emissions from petroleum combustion, and (3) maintain energy security by displacing a major portion of the transportation fuel requirement with a clean fuel produced from indigenous U.S. resources.

Additional needs of the SERDP program will be met in the thrust area of Pollution Prevention: (i) reduction of greenhouse gas emissions in response to concerns about global warming, and (ii) reduction of solid waste resulting from trash/construction, water treatment. The latter need will be addressed by demonstrating the use of waste materials from military installations as feedstock including rubber tires, fabrics, water treatment sludge and other carbonaceous wastes that would otherwise require disposal in landfills. The clean liquid fuel thus recovered will displace petroleum and reduce greenhouse gas emissions (i.e., methane) from landfills.

7. Project Description:

The proposed process was conceived at the Brookhaven National Laboratory (BNL) and has been under evaluation by EPA/AEERL since 1990 in cooperation with BNL. The evaluations include feasibility studies, laboratory experimental studies, process simulations, and economic assessments, the results of which were peer-reviewed during 1993 by a panel of 8 extramural scientists and independently by the EPA Science Advisory Board. With concurrence of these reviews, the process evaluation has progressed to the design of a 50-lb/hr pilot test facility, completed in August, 1993, under cosponsorship of the California South Coast Air Quality Management District. The first phase of construction of that test facility will be undertaken with SERDP funds awarded in FY93. The project will be accelerated and completed in a four-year period with the funds currently proposed.

The process consists of three basic steps: a hydrogasifier, a methane conversion reactor, and a methanol converter. The unique features of the process that improve upon other gasification systems are the use of natural gas a cofeedstock and the recycle of excess hydrogen derived from that natural gas to the gasifier. Because biomass contains insufficient hydrogen to convert all of its carbon to alcohol, these improvements markedly enhance the alcohol yield and reduce the cost of production. Addition of natural gas provides a source of extra hydrogen that permits complete conversion of the carbon and the addition of steam further increases alcohol production. When the excess hydrogen is recycled to the gasifier, alcohol yield is again leveraged due its reaction with carbon dioxide to form the methanol precursor, carbon monoxide; other biomass conversion processes must purge nearly half of the biomass-derived carbon as carbon dioxide, greatly reducing the potential alcohol yield. Because of these two advantages of the proposed process, economic comparisons show that it will have lowest cost per unit of fuel energy and larger impact on displacement of petroleum imports than any other process option, or combination of options, that could achieve equivalent reduction of greenhouse gas emission from mobile sources.

The process has two basic operating configurations. The first configuration to be demonstrated is applicable to feedstocks consisting carbonaceous materials such as those comprising much of the waste from military installations. Tests of such materials constitute the first objective of the project, which will involve the following critical elements: (1) construct and test a biomass gasification reactor and gas cleanup system, designed to operate at the required temperature and pressure, (2) construct and test a methane reformer designed to react the gasifier effluent with steam and natural gas, and (3) integrate these reactors with a methanol converter and recycle system to establish the feasibility of duplicating the performance predicted by theoretical process simulations. The critical path to successful demonstration requires testing of each reactor in an uncoupled mode followed by testing of an integrated system of the three process steps using water scrubbing for gas cleanup prior to the reforming step.

The second process configuration is applicable only to woody biomass as feedstock. This biomass would be produced on dedicated energy plantations in the manner being developed by the Oak Ridge National Laboratory for the specific purpose of conversion to liquid fuel on a large scale. For this purpose, the test facility will utilize a hot-gas cleanup system instead of a wet scrubber, which will improve thermal efficiency and achieve greater net reduction of greenhouse gas emissions. Each of the two reactor configurations will be evaluated in extended series of parametric tests that will demonstrate technical feasibility and provide data over a broad range of operating conditions for engineering design and process scaleup. All individual components of each process configuration are within the state-of-the-art of various existing commercial processes.

8. Expected Payoff:

Evaluations by EPA have shown that methanol can reduce VOC equivalent emissions by 80 percent, producing 40 percent less ozone per vehicle mile, and reduce the risk-weighted toxics emissions by 90 percent per vehicle mile. Methanol can increase thermal efficiency by 30 percent relative to gasoline in internal combustion engines. The DOE national Energy Strategy of 1991/92 concluded that an alternative fuel of some kind will be needed in large amounts by the year 2000 due to declining petroleum reserves. Specific requirements for identifying the best alternative fuel for broad use were outlined in the Energy Policy Act of 1992, which established a goal of 30 percent displacement of petroleum by the year 2010. According to the Act, the desired alternative should have maximum displacement of oil imports, greatest benefit to the national economy, and minimum greenhouse gas emissions. These goals imply that the selected process for alternative fuel production should utilize indigenous resources as feedstock and obtain maximum yield of clean fuel from those resources. Evaluations of the technological options have shown that the proposed process, if successfully developed, can achieve 13 percent greater displacement of petroleum and 45 percent greater reduction of greenhouse gas emission than the best alternative combinations of processes that might convert the same total resources to liquid fuels. They further show that these results should be achieved at no incremental cost relative to the equivalent price of gasoline displaced.

If successfully developed, the process could provide, from secure indigenous resources, a large part of the military fuel requirements which will otherwise compete increasingly with the needs of the public sector. At the same time, the problem of waste disposal from military installations--such as rubber tires, discarded fabrics and spent organic wastes--will be reduced by conversion of much of the waste to clean fuel.

9. Milestones:

1.	Finalize design of biomass gasifier	10/93
2.	Prepare specifications and equipment lists	10/93
3.	Issue purchase requests for gasification reactor (EPA)	04/94
4.	Begin construction of gasification reactor	07/94
5.	Begin design of methane converter	07/94
6.	Complete construction of gasifier	09/94
7.	Complete gasifier tests with wood and natural gas	11/94
8.	Review final design of methane converter	11/94
9.	Construct Phase I gas cleanup system	01/95
10.	Construct Phase I methane conversion reactor	02/95
11.	Design methanol converter	04/95

12. Complete tests of methane conversion reactor 06/95
13. Review test plan for integrated system 07/95
14. Complete construction of methanol converter 09/95
15. Complete tests of Phase I configuration with wood and natural gas cofeedstocks 11/95
16. Begin feedstock tests on military carbonaceous wastes 11/95
17. Complete tests of waste feedstocks 02/96
18. Review and evaluate Phase I testing 03/96
19. Design hot gas cleanup system for Phase II 04/96
20. Review Phase II methane converter design 05/96
21. Complete installation of Phase II system 07/96
22. Complete testing of Phase II configuration 09/96
23. Complete parametric tests on integrated system 12/96
24. Review Phase II results 01/97
25. Conduct engineering studies for scaleup 03/97
26. Complete final report 06/97

10. Transition Plan:

The proposed test facility is the smallest system that could provide useful information on the potential of the process. If successful, further evaluation on a process development unit (10 tons/day) and a process engineering unit (100 tons/day) will be needed for final scaleup and accurate assessment of performance and cost. It is clear that the private sector has no current incentive to develop methanol as an alternative to petroleum--the true cost of which is heavily subsidized by the public sector. It is essential therefore, if the best alternative fuel is to be made available in amounts needed to meet national strategic and economic goals most effectively, that process development begin now. Support by DoD for the initial development phase of this process should enhance the prospects for attainment of a secure supply of fuel to meet its requirements as well as assisting the public and private sectors with the development of technology to meet the future needs of both. A successful pilot demonstration with DoD support will greatly improve the prospects for early involvement by the petroleum industry for scaleup to a level that will significantly affect national transportation fuel requirements.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	500	500	400	400	200	2000
EPA	425	375	375	375	375	1925
BNL	30	30	30	20	20	130
TOTAL	955	905	805	795	595	4055

12. Performers:

In accordance with letters of intent to be submitted with this proposal, we anticipate that the test facility will be located in the proximity of, and supported by, the March Air Force Base and the Palms U.S. Marine Supply Depot, both located in Riverside County, California. The letters also express the continued support of the California South Coast Air Quality Management District and the California Energy Commission for this project as a new technology for domestic

methanol production for the District's Clean Fuels Program. Brookhaven National Laboratory will continue to contribute substantial in-kind engineering design and process simulation services. EPA will cofund the project through funding from the Federal Coordinating Council for Science, Engineering and Technology's Advanced Manufacturing Program. AEERL will provide the full-time chemical engineering support of the principal investigator.

13. Principal Investigator:

Robert H. Borgwardt (MD-63)
USEPA, AEERL
Research Triangle Park, NC 27711
Phone: (919) 541-2336
FAX: (919) 541-2382

14. Keywords:

Alternative fuels, greenhouse gas, methanol, biomass, global warming, carbonaceous wastes.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Utilization of Biomass Technologies on Military Installations

3. **Agency:** U.S. Environmental Protection Agency (EPA)

4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)

5. **Proposal ID:** #227

6. Problem Statement:

The goal of this project is to determine the technical, economical, and environmental feasibility of small innovative energy conversion technologies fueled with biomass. The DoD, and numerous other institutions, operates a large number of small energy conversion systems that burn fossil fuels and are in need of repair or replacement. These systems emit substantial amounts of air pollutants (SO_2 and particulate) which must be controlled. Installing biomass fueled systems or converting or replacing existing equipment with systems that utilize biomass would eliminate SO_2 emissions, produce zero net gain of CO_2 emissions, reduce air toxic emissions, and reduce waste disposal problems. The objective of this project is to demonstrate, test, and evaluate a biomass fueled innovative energy conversion technology at a DoD installation. The research category for this project is applied research, and technology demonstration and technology transfer. This project is an enhancement to the previously SERDP funded (FY93) project and continues to be an opportunity for the DoD, EPA, DOE, USDA, AID, national labs, and industry to cooperate in demonstrations that will benefit each organization.

7. Project Description:

The technical objective of this project is to demonstrate that small innovative energy conversion technologies fueled with biomass are technically, economically, and environmentally feasible for DoD installations, industries, and developing countries. Existing efforts have focused on large scale systems or mature technologies. The small scale innovative energy conversion technologies have been neglected. The technical approach for this project is to identify interested DoD sites (many military installations have expressed interest and two have offered to be a host site -- see attached letters), identify the project cooperators, select the most viable technology, and design, build, and test the system. The coordination between DoD and cooperators would be such that the design of the project would be in the best interest of the host DoD installation. The biomass fuel supply would be generated by activities on-site, in the community, and/or from dedicated feedstock supply systems (DFSS). The technical risks would be minimized by the proper selection of technology based on the available site, size of system, type of fuel, qualifications of operators, and lessons learned by all cooperators. The project would build upon the EPA/OPPE and DoD study "Enhancing Management of Forests and Vegetation on Department of Defense Lands: Opportunities, Benefits, and Feasibility;" the EPA/AEERL, Southeast and Southwest Regional Biomass Energy Programs, DOE, and National Wood Energy Association funded Sutton/Energeo and Cratech biomass-to-energy projects; the EPA/AEERL, DOE, and AID biomass integrated gasification/gas turbine study; the EPA/AEERL multi-fuel combustor research; the EPRI Distributed Generation Study; the USDA work with a wood fired combustion turbine, utilization of wood pallets and marketing of cull trees; the NREL gasifier scale-up in

Hawaii; the Western Research Institute work with co-firing wood and coal in a turbine; the Regional Biomass Program for utilization of biomass; and ORNL research in DFSS. The project relates to the needs of the DoD by supporting Pillar 3 of the Tri-Service Research Plan, Thrust 3.M: Reduce greenhouse gas emissions, (3.V.2.d) Improve efficiencies of mechanical systems and (3.V.3.a) Alternative/renewable energy sources and the DOE by supporting Title XII: Renewable Energy of Energy Policy Act of 1992, H.R. 776/Public Law 102-486, direct combustion or gasification of biomass and biofuels energy systems.

8. Expected Payoff:

After successful demonstrations, energy conversion technologies fueled with biomass could be applied in developed or developing countries, industrial sites, rural areas, as well as, DoD installations. The technologies could be modularized to allow for varying fuel supplies, energy demand, and transportability. The benefits for the DoD to install biomass fueled systems are 1) reduce air emissions, 2) minimize on-site and community biomass waste disposal, 3) savings from tipping fees, purchase of fossil fuels, and electricity, 4) energy security at domestic and international military installations, and 5) promotion of exportable technologies.

9. Milestones:

1.	Finalize Cooperative Agreement Solicitation	09/93
2.	Receive and evaluate preproposals	01/94
3.	Award Competitive Cooperative Agreement	04/94
4.	Identify site/energy needs/existing system/fuel supply	05/94
5.	Identify various technologies	06/94
6.	Select appropriate technology	08/94
7.	Establish partnerships	08/94
8.	Define contributions and responsibilities of partners	09/94
9.	Assist with design of system	09/94
10.	Begin construction	10/94
11.	Begin testing and evaluations system	03/95

10. Transition Plan:

The amount of government/industry cooperation required for a project of this type should lead to future CRADA's between government and industry. This project would provide the jump start needed for the development of equipment, design of systems, creation of new markets, and realization of existing untapped markets for biomass fueled energy conversion systems. The potential systems will be comprised of off-the-shelf components or components manufacturable by existing industries. A successful demonstration would allow developing countries to get approval for financing from multi-lateral lenders. Developing countries are in dire need of this type of technology because biomass waste is both a disposal and air pollution (open burning) problem and diesel fuel is too costly to import. Biomass fueled technologies will help provide sustainable energy without being detrimental to the environment.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	750	750	750	750	750	3750

12. Performers:

Demonstration of energy conversion technologies utilizing biomass will be performed through the cooperation of the EPA, DoD, DOE, USDA, AID, national labs, and industries. The DoD will provide the demonstration site, specific information to aid the technology selection process, and possibly system operators. The EPA/AEERL will provide coordination of project management and engineering, evaluation of technologies to be considered, and evaluation of environmental and site specific data. The DOE/NREL will provide expertise in the technology selection process. The Regional Biomass Programs, USDA Forest Service, and ORNL will provide off-site resource information, including DFSS. Industry will provide system development/design and hardware depending on the technology selected. AID/Winrock will examine opportunities for transferring technology to international markets.

13. Principal Investigator:

Carol R. Purvis (MD-63)
USEPA, AEERL
Research Triangle Park, NC 27711
Phone: (919) 541-7519
FAX: (919) 541-2382

14. Keywords:

Biomass-to-Energy, Energy Conversion, Combustion, Gasification, Gas Turbine, Distributed Power Generation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Low Emissions Shipboard Fuel Cell Power Plants

3. **Agency:** Navy

4. **Laboratory:** CDNSWC Annapolis

5. **Proposal ID:** #047

6. **Problem Statement:**

Ship Air Emissions Reduction / Energy Conservation

Fuel cell power system technology has advanced rapidly in the last 5 years, primarily because fuels cells are essentially non-polluting and efficient. The DoD, is the single largest user of energy in the world with an annual energy consumption of 150 million barrels of oil with a yearly cost of $3.32 billion. Judicial use of fuel cells will enhance the DoD goal of reducing energy consumption by 20 percent by the year 2005, reducing all emissions, and to conserve the strategic petroleum reserve. The Clean Air Act of 1990 set minimum standards for states in controlling air pollution, and gave states the authority to enact more stringent air emission regulations. A proposed California regulation would restrict NO_x and SO_x emissions from marine diesel and gas turbine engines within 100 NM of the southern California coast. This regulation and others likely to follow could severely impact fleet operations. Furthermore the anticipated ratification of MARPOL Annex 6 and its follow-on implementation by Congress could impose severe operational limitations on engine emissions in coastal regions and "special areas" around the world -- severely impacting foreign ship operations. The potential cost to the Navy for real or perceived non-compliance will be very high. These emission regulations will apply to auxiliary generators as well as main propulsion systems on all ships. This project addresses the issues necessary to reduce DoD energy consumption and to achieve environmental compliance, through the use of fuel cells for shipboard electric power generation.

7. **Project Description:**

Fuel cells are being developed for utility applications primarily because they are efficient and friendly to the environment. This project directly supports Requirement 2-I1.i of the Tri-Service Environmental Quality R & D Strategic Plan; i.e, Control Emissions from Ship Propulsion Systems. This requirement also applies to shipboard auxiliary power generators.

Fuel cell technology provides policy makers with an option which greatly exceeds the present air pollution regulations-even the rigorous ones evolving in California. In addition fuel cell technology provides one of the few strategic options to reduce CO_2 emissions. Fuel cells utilize electrochemical reactions between hydrogen and oxygen to produce electricity; high temperature fuel cells also consume CO as a fuel. The hydrogen is obtained by catalytically or steam reforming fuels. In this process high temperature combustion of fossil fuels are avoided, so that electricity is produced without smoke.

To date no fuel cell has been operated on diesel fuel, however diesel fuel processing equipment is being developed under the Navy 6.2 program. The technical objective of this project is to demonstrate that fuel cell power systems operating on diesel fuel will provide acceptable shipboard emissions for both Navy and maritime service, and enhance fuel conservation. Fuel cells, being electrochemical in nature, produce less than 10 ppm of NO_x, and near zero CO. The amount of SO_x emitted by any power source is directly proportional to the amount of fuel used and the amount of sulfur in the fuel. Fuel cells, being more efficient than either diesels or gas turbines, will have significantly lower SO_x and CO_2 emissions.

Breadboard 10 kW fuel cell systems will be initially used to demonstrate the non-polluting feature of fuel cells when operating on diesel fueled marine duty cycles and to verify efficiency predictions. Following successful demonstration at the 10 kW level, a nominal 250 kW marine power system design will be developed and demonstrated for one or more fuel cell technologies. This power level which is compatible with future ship electric system requirements, is a cost effective level to demonstrate the modular technology, and can be used to support a variety of dual use marine applications. Some examples are auxiliary power for patrol boats (USCG Cutters), small combatants, auxiliary vessels, commercial fishing boats and cruise ships. The Alaska Energy Authority has also expressed interest and has agreed to cost share in part of this effort.

The first demonstration will involve operating a DOE-owned 10 kW molten carbonate fuel cell stack on diesel fuel for 400 hours. Successful operation of a smaller molten carbonate (700 W) fuel cell on EXXSOL D110 fuel was demonstrated for 600 hours, under a NAVSEA 03R SBIR contract with Arctic Energies LTD. The liquid fuel, which is similar to diesel fuel, was first converted to a methane rich gas mixture, which was then further reformed inside the fuel cell stack. It is planned to measure the exhaust composition under a variety of marine operating conditions and to obtain additional process design information. A nominal 250 kW system design will be developed to be used in a follow on demonstration of a molten carbonate fuel cell suitable for installation on a naval vessel. It is planned to conduct this work using SERDP funds by implementing a Phase 3 to the existing NAVSEA SBIR contract with Arctic Energies LTD.

A second demonstration will be conducted utilizing a 10 kW proton exchange membrane (PEM) fuel cell system being developed by Analytic Power Corporation under ONR Surface Ship Technology Program. The system consists of a diesel fuel autothermal reformer, a low cost, high power density PEM fuel cell stack, and associated auxiliaries. Proper operation of the hardware will be demonstrated using Navy funds in FY 94. Tests will then be conducted under this SERDP task to measure the diesel fueled plant exhaust composition under a variety of marine operating conditions. This program complements the Army program to develop fuel cells for military applications, in which CDNSWC is participating by providing sites for evaluation of phosphoric acid power plants for utility use. The potential for technology transfer between the Army and Navy is extremely high. This program addresses aspects which are unique to Navy and maritime application of fuel cell technology. Requirements for naval applications differ significantly from utility requirements. The primary differences are the use of a logistic fuel, and the need for a higher power density. Maximum use is being made of previous DOE fuel cell technology, but the emphasis will be placed on the adaptation of this technology to marine applications. At this stage of development, the ONR 6.2 program is evaluating fuel cell technologies to determine their potential for marine service, and is currently supporting R & D on fuel cells. This proposal is limited to the molten carbonate and PEM technologies, since experimental power plants and test facilities exist. The molten carbonate technology, while currently having a low power density, has a high efficiency and is being commercialized. The

PEM technology operates at a lower efficiency, but has a high power density and is being developed for transportation applications. During FY 95 and 96 one or both 250 kW fuel cell plants will be developed with testing to follow giving special attention to marine power source requirements. Competitive procurements are planned for these power plants, which will be evaluated by marine engineers.

8. Expected Payoff:

A recent ship impact study conducted by CDNSWC for ONR concluded that a fuel cell powered ship over its 30 year life will emit 96 % less NO_x, CO and hydrocarbons than a conventional gas turbine system. This study also showed that fuel cell power systems save between 12-15 % of ship propulsion fuel, and up to 20 % of the fuel required for generating ship service power for a naval combatant. This also means that the amount of SO_x and CO_2, both of which are greenhouse gases, are reduced in the same proportion.

The expected payoff to the Navy and Maritime industry is reduced fuel consumption due to higher efficiency fuel cell systems, and the likely ability to meet all known future environmental requirements. Use of fuel cells on ships and military bases directly conserves the strategic petroleum reserve. Since all fuel cells essentially consume hydrogen, they can use alternate fuels such as methanol and ammonia for example. It is even feasible convert shipboard waste into gases suitable for use in a fuel cell, which in the long term will further reduce emissions and conserve petroleum reserves.

9. Milestones:

This program leverages technology developed under previous Navy SBIR contracts and the ONR 6.2 program. Milestones 1-4 are possible due to advances made under these programs.

1.	Publish results of 400 hr test of 10 kW Molten Carbonate fuel cell operating on Diesel Fuel.	06/95
2.	Complete Preliminary Design of 250 kW Molten Carbonate fuel cell system for marine applications.	08/95
3.	Publish results of 10 kW diesel fueled PEM fuel cell evaluation, including efficiency and emissions data.	06/95
4.	Complete Preliminary design of 250 kW PEM System for marine applications.	08/95

Following completion of Milestone 4 and analysis of the results by Navy power generation experts and naval architects, it is proposed milestones 5, 6 and 7 be accomplished under the SERDP 6.3A with support from the Navy 6.2 program.

5.	Award Contract(s) for 250 kW System Fabrication	04/96
6.	Complete fabrication of 250 kW systems.	10/97
7.	Complete Navy evaluation of 250 kW systems.	03/99

10. Transition Plan:

ONR sponsored ship impact assessments have shown that fuel cells can provide low signature, non-polluting ship power without significant impact on the ship size or cost. Fuel cell technology has been recently identified by NAVSEA as one of thirty technologies that have

potential for application in the 21ST Century Destroyer program. The 250 kW systems being developed here support the modular power plant design approach expected to be use in the future combatants. We propose that a combination of Navy and SERDP 6.2 funds be used for the 10 kW demonstrations and development of 250 kW systems. Part of the 10 kW molten carbonate tests will be funded by the Alaska Energy Authority (AEA). These steps, which will demonstrate fuel cell operation on diesel fuel, and provide additional information on system weight, volume and efficiency, are considered critical to successful development of fuel cell power systems for the Destroyer, ca. 2003. The design specifications and technology developed under this effort have considerable dual use applications, such as providing power for Coast Guard vessels, cruise ships, and other mobile applications.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	0	600	3000	3000	1030	700	300	8630
NAVY 6.2	420	445	550	600	500	0	0	2515
AEA*	0	28	0	0	0	0	0	28
Total	420	1073	3550	3600	1530	700	300	11173

* State of Alaska, Alaska Energy Authority

Notes: 1. FYs 95/96: include the purchase of two 250 kW systems
2. Portions of the 6.2 funding will be used to develop relevant advanced technology, e.g. sulfur adsorption systems, solid oxide fuel cells, and additional ship impact studies.

12. Performers:

The planned FY 94 performers are CDNSWC, Arctic Energies LTD, and Analytic Power Corporation. Arctic Energies, under a Phase III NAVSEA SBIR, will be responsible for conducting the 10 kW molten carbonate fuel cell operation on diesel fuel and for providing a preliminary design for a 250 kW system. Analytic Power Corporation will be responsible for evaluating the PEM system, and for providing a preliminary design for a 250 kW system. CDNSWC will manage both efforts and preform inhouse design and application studies to guide the Navy's fuel cell development efforts, and procure the 250 kW systems competitively. CDNSWC will manage development and test of the 250 kW systems and be responsible for coordinating this development with other interested agencies. Arctic Energies LTD recently completed a NAVSEA sponsored SBIR contract on which the molten carbonate portion of this work is based. Arctic Energies also has conducted several studies relating to the use of fuel cell in naval applications. Analytic Power Corporation has developed a 10 kW diesel fuel operated proton exchange fuel cell for the Navy, which includes an autothermal reformer, and a complete balance of plant, including a regenerable sulfur absorbent bed. CDNSWC directed these and other fuel cell developments, and completed an extensive study to determine the impact of this technology on surface ship performance.

13. Principal Investigator:

Joseph A. Woerner
Annapolis Detachment, Carderock Division
Naval Surface Warfare Center, Code 824
3A Leggett Circle
Annapolis, MD 21402-5067
TEL: 410 293-2148
FAX: 410 293-3553

14. Keywords:

Fuel Cells, Energy, Emissions, Air Pollution, Thermal Efficiency, Diesel Fuel

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources

2. **Title:** Photovoltaics for Military Applications

3. **Agency:** Navy

4. **Laboratory:** Navy: NAWCWPNS China Lake

5. **Proposal ID:** #046

6. **Problem Statement:**

This is a joint proposal from the Department of Defense (DoD) Photovoltaic Review Committee (PVRC), and the Office of Naval Research and the Department of Energy (DOE). The DoD PVRC and DOE jointly executed FY91 and FY93 SERDP activities, and continue to be strongly committed to a joint program.

The program goal is to support and accelerate existing DOE and DoD alternate energy programs to reduce the operational and cost impact of meeting environmental obligations in the DoD and to transfer that technology and information to both the federal and private sectors for widespread implementation.

DoD is the largest single user of energy in the world with annual pollution emissions estimated at 720 million tons of CO_2, 1.15 million tons of NO_x, and 740,000 tons of SO_x. The potential PV application base within DoD is estimated at 50+ MW for small remote systems (less than 25 kW), 200+ MW for intermediate to large remote systems (25 - 1000 kW), and 450+ MW for large grid interactive systems (greater than 100 kW). Small stand-alone systems for the DoD are considered mature and proven. This program targets intermediate to large remote systems and grid interactive systems for remote "island" grids that generate their own power and for load leveling and uninterruptible power for large utility grids.

Program objectives are to leverage DOE's development of innovative PV technologies by demonstrating them in high value applications within DoD. These objectives will reduce emissions to comply with regulations, make progress toward installing 100 MW of renewable energy projects in DoD as directed by the National Defense Authorization Act, help reduce CO_2 emissions, and maintain energy security by reducing dependence on fossil fuels thereby conserving the strategic petroleum reserve. The program is integrated with the PVRC's "fenced" PV Energy Conservation Investment Program (ECIP) and DOE's Balance-of-Systems and Government Agencies PV initiatives to avoid any duplication of effort.

The research category is 6.3. The primary focus will be the integration of existing research/technologies into systems and demonstration in selected field installations thereby preparing the technology for widespread transfer and implementation to the federal and private sectors. The program is a continuation of the joint DoD/DOE FY91 and FY93 Phase I and III projects.

7. Project Description:

The program includes three tasks: 1) Application Evaluation, 2) Hardware Development, and 3) Application Validation. SERDP and ECIP projects are evaluated and selected under Task 1. The FY91 effort initiated a comprehensive data base which will characterize all DoD energy systems, identify potential PV projects, and document the history of projects implemented under ECIP and SERDP. This data base is used to determine energy priorities and needs, and to enhance access to project information and promote information exchange. Projects that meet DoD priorities and needs, are replicable throughout DoD, and expand the PV application base are identified and ranked by the PVRC and SNL. The top ranked projects are evaluated to determine system requirements, specify hardware, and estimate cost and environmental savings. As part of this program, the EPA is developing techniques to quantify the environmental savings. The projects are implemented in order of their ranking. All project information is documented in the data base and widely disseminated.

Any hardware specified under Task 1 that is not off-the-shelf technology is developed under Task 2 through engineering contracts to manufacturers. This effort focuses on integrating existing components and capabilities into field worthy packages. The FY94 effort will use advances from the BOS initiative to develop integrated power processing and control hardware that will operate in both a stand-alone mode (as a voltage source) and in parallel with other sources (as a current source) to serve all potential applications. Out-year development will focus on balance-of-system requirements to use advanced PV collectors, including thin films (multi-junction amorphous Si, $CuInSe_2$, CdSe/Te) and concentrators, as they are validated through the DOE program. These lower cost technologies will expand the application base for PV within DoD. Beyond PV collectors, the development will investigate PV compatible alternative energy storage to eventually displace diesel fuel and batteries and avoid their negative environmental consequences. One alternative that will be investigated is hydrogen because it is environmentally benign and can be generated on-site by PV-driven electrolysis.

The applications and systems are validated through demonstrations at DoD facilities. After installation, the systems are evaluated for acceptance and to determine a baseline performance rating. The systems are then evaluated yearly, throughout the life of the program, to develop a technology track record, establish O&M requirements, and identify design improvements.

This approach has now resulted in 8 intermediate size PV systems in various stages of implementation. Seven of these are PV/diesel generator hybrids including one at an electronic warfare range on San Clemente Island (REWS), two at radar facilities at China Lake (Junction Ranch and Shipsite), an artillery range at 29 Palms (Range 500), air combat ranges at Mt. Home Air Force Base (Grasmere Point) and China Lake (Superior Valley), and a mobile power center (MPC) for the Marine Corps. The stationary systems are designed for capacities between 100-200 kW with PV arrays from 50-100 kW. The MPC is designed to replace 10 kW mobile generators. The 8th project is a grid interactive system at Yuma Proving Grounds (Yuma) for demand charge reduction designed for 150-200 kW capacity with 150-200 kW of PV. These projects are on schedule for installation in 1994. The joint efforts of the PVRC and SNL has been a key element in the progress achieved thus far.

Technical risks of the program are moderate. The program is structured to phase in advanced technology so that the majority of the system uses mature technology. Advanced technology is tested and evaluated as necessary at an independent facility before installation. The critical path elements within the program are 1) technical maturity of advanced PV collectors and alternative

energy storage, 2) project approval and system procurement, and 3) coordination with the supplier to test non-mature hardware. These risks will be minimized by project phasing based on technology maturing, close interaction with the user, and aggressive project scheduling and execution.

8. Expected Payoff:

If successful, this program will establish viable electrical generation and energy storage technology for widespread applications with the expertise within DoD to implement the technology where appropriate. The long-term benefits include both substantial environmental savings, economic savings, and reduction in consumption of fossil fuels. Current estimates of potential annual savings by using PV are 433,000 tons CO_2, 10,123 tons of NO_x, 450 tons of SO_x, $495 million. Estimated energy generation indicates that PV can reduce dependence on fossil fuels by 800,000 MWh of electricity per year. PV can also substantially reduce the hazards associated with the transport and handling of liquid fossil fuels as diesel generators are phased out, increase mission capability and reliability, and increase energy security. Note that these benefits will be quantified for all SERDP and ECIP project. The technologies and applications developed and demonstrated under SERDP have direct application and leverage to other government agencies including the National Park Service and National Forest Service. For example, SNL is working with the National Park Service to survey all their diesel generators to examine the potential for cost and environmental savings through PV. There are also a number of near-term benefits beyond the immediate savings provided by the systems themselves. SERDP will provide a means to apply advanced technologies from DoD, DOE, and the private sector, expand the application base for U.S. products and enhance the capability of industry to service these applications, transfer information on the technology and it's capabilities throughout DoD, and provide utilities a model for use of PV in "island" grid and value-added utility grid applications.

9. Milestones:

1.	Complete stand-alone/parallel integration/procurement	01/95
2.	Install and evaluate stand-alone/parallel system	01/96
3.	Complete advanced collector (1) integration/procurement	01/96
4.	Install and evaluate advanced collector (1) system	01/97
5.	Complete new collector/BOS (2) integration/procurement	01/97
6.	Install and evaluate advanced collector (2) system	01/98
7.	Complete advanced collector (3) integration/procurement	01/98
8.	Install and evaluate advanced collector (3) system	01/99
9.	Complete alternative storage integration/procurement	01/99
10.	Install and evaluate alternative storage remote system	01/00
11.	Install and evaluate alternative storage utility system	09/00
12.	Complete evaluations and documentation of system history	09/01

10. Transition Plan:

SERDP, as well as ECIP, are integral parts of DoD's Photovoltaic Master Plan, developed and documented by the PVRC, to bring about the use of photovoltaics where appropriate and cost-effective. The overall goal of the plan is to realize the full potential of PV in all DoD applications from small remote to intermediate and large hybrids to value-added utility interactive. The Master Plan details a three-pronged strategy to achieving this goal through Outreach, Logistic

System Conditioning, and Project Development. Outreach activities are designed to expand the general awareness and knowledge of PV technology and its capabilities. Logistic System Conditioning is designed to integrate PV into the established Federal logistics system to make the procurement of PV systems routine. Project development is designed to identify replicable applications throughout DoD and aid the user in developing the technical and institutional conditions necessary to turn those applications into reality. In addition to the technical aspects, project development activities also investigate other financing avenues like third party capital venture and power purchase/lease agreements with suppliers and utilities.

Project Development activities are used to affect the transition of PV technology from advanced development (6.2/6.3) through engineering development (6.4) to full implementation. SERDP funds provide the vehicle for the transition from advanced to engineering development by demonstrating and validating advanced technologies and applications. "Fenced" ECIP funds provide the vehicle for the transition from engineering development to full implementation by demonstrating that the application is cost-effective and that the technology and industry are prepared for full implementation. Once an application and technology have completed the SERDP and "fenced" ECIP phases, it can be implemented where appropriate through regular ECIP/MILCON or commercial channels.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	4000	4000	4000	4000	250	250	16500
ECIP	0	5000	5000	5000	5000	5000	25000
DoD	800	800	800	800	0	0	3200
DOE	50	150	200	200	0	0	600
Total	4850	9950	10000	10000	5250	5250	45300

NOTE: Outyear funding reflects requested SERDP funding and anticipated ECIP funding. Outyear funding for DOE and DoD is unknown.

12. Performers:

The program is managed by the DoD PVRC chaired by Garyl D. Smith of the Office of Naval Research (Code 464/12E) and DOE's Photovoltaics Technology Division, directed by James E. Rannels. Technical work is performed by SNL's Photovoltaic Projects, managed by Dr. David Hasti, and the PVRC with contract support from the Global Warming Control Branch of the EPA, Southwest Technology Development Institute, and the Meridian Corporation. DoD facilities that sponsor projects provide substantial support for project development and system procurement. All systems will be supplied by U.S. PV industry through competitive contracts. Although they are not specifically excluded, there are no formal Cooperative Research and Development Agreements (CRADA) contemplated.

13. Principal Investigators:

Garyl D. Smith
Chairman, DoD Photovoltaic Review Committee
Energy Programs Office
Code C8303
Naval Air Weapons Station
China Lake, CA. 93555
Tel: (619) 939-2525
Fax: (619) 939-7366

Dr. David E. Hasti
Photovoltaics Projects Manager
Division 6218
Sandia National Laboratories
P.O. Box 5800
Albuquerque, N.M. 87185-5800
Tel: (505) 844-8161
Fax: (505) 844-6541

14. Keywords:

Photovoltaics, renewable energy, diesel generators, energy storage, hybrid, utility interactive.

TABLE A-V **FY 1994 GLOBAL ENVIRONMENTAL CHANGE PROJECTS**	**Funding $(K) FY94**	**ID Number**	**Page Number**
Air/Ocean Interface Research			
Global Ocean Monitoring and Prediction (GOMAP) (N)	900	18	A-357
Atmospheric Research			
Comparison of CIRRIS 1A and UARS/ATMOS Databases (AF)	395	100	A-362
Environmental Requirements for Cloud Analysis (AF)	800	98	A-365
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE) *	24,700	470	A-370
Ocean Research			
Acoustic Monitoring of Global Ocean Climate (includes GAMOT) (ARPA) *	17,000	286	A-375
Terrestrial Research			
Global Inventory of Biomass Burning (EPA)	600	238	A-380
Other			
Strategic Environmental Distributed Active Archive Resources (SEDAAR) (N) *	1,250	816	A-386
Global Environmental Change Total	**45,645**		

* Congressional Interest

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Global Ocean Monitoring and Prediction (GOMAP)

3. **Agency:** U.S. Navy

4. **Laboratory:** Naval Research Laboratory (NRL)

5. **Proposal ID:** #018

6. **Problem Statement:**

The basic thrust of this proposal is Global Ocean Monitoring and Prediction (GOMAP) at a resolution sufficient to depict features such as oceanic fronts and eddies. This effort will cover both deep and shallow water and use a combination of numerical ocean models, remotely sensed data and in situ data to develop ocean and ocean/atmosphere interface models aimed at predicting the natural variability of the global ocean system and its effect on short and long term climate variability. It includes atmospheric wind and heat flux forcing which is essential for the ocean models.

One major aspect of this research is determining the origin of observed oceanic anomalies and understanding their dynamics using a combination of global satellite data, an eddy-resolving global ocean model and a comprehensive coastal model. The identification and understanding of the natural variability of the global ocean system are important components in understanding both short and long term climate variability. Under this effort we will also investigate the ability of the models to predict the evolution of different types of anomalies and their time scales for predictability. For example, NRL recently demonstrated for the first time: (1) that verifiable decadal ocean anomalies can be seen in the 5-year change in sea surface height (SSH) obtained using satellite altimeter data from the Geosat-Exact Repeat Mission (Geosat-ERM) and ERS-1 and using techniques developed by proposed project members; (2) that the NRL global ocean model can simulate these anomalies when driven by operational atmospheric forcing; and (3) that the NRL model can be used to determine the origins and dynamics of such anomalies. One prominent anomaly (high SSH and warm sea surface temperature, SST) spanned the North Pacific from Japan to Alaska in 1992-93 as seen in the altimeter data, the model results, and SSTs from satellite IR. Using the NRL model it was possible to determine that this anomaly stemmed from the 1982-83 El Nino a decade earlier! It was also possible to determine the underlying dynamics which included a Rossby wave that lasted a decade and crossed the entire Pacific (an event not previously observed). It is notable that the anomaly was maintained by the model and propagated to the observed location over a period of 10 years without oceanic data assimilation. In this project other anomalies of interest would include heat transport; inter-basin exchanges of momentum, heat, salt and bio-optical properties; shallow water-deep water exchanges; and the identification and study of regions of isopycnal ventilation. Since the NRL global ocean model is truly eddy-resolving (1/8 degree resolution, the highest available), it can include critical eddy processes in calculations of global ocean heat transport and can be used for regional applications in the context of time dependent influences of the larger scale circulation.

This effort will also develop an eddy resolving GOMAP system. This includes: (1) enhancing the existing NRL effort aimed at assimilation of satellite and in-situ data into the NRL 1/8-

degree, eddy-resolving global ocean model; (2) accelerating efforts aimed at coupling the global and coastal models and developing data assimilation in shallow water; (3) assessing the impact of satellite and in-situ data of different types on our ability to synoptically describe the ocean circulation and monitor anomalies; (4) assessing the impact of using the ocean models to assimilate the data as opposed to analyses of the data alone; and (5) using the ocean models in observing system design. Ocean models are essential for effective synthesis of abundant remotely-sensed global surface data to: (a) fill in space-time gaps in the data; (b) convert data on the location of oceanic fronts into more quantitative 3-D information (NRL has developed techniques for doing this); (c) convert abundant surface information into subsurface information which is sparsely observed (NRL has also developed effective means of doing this); and (d) convert better-known atmospheric forcing into oceanic information as was done in the study of the decadal impact of the 1982-83 El Nino. One major objective of this project will be to provide a continuous synthesis of global/regional model + satellite data results spanning a decade at 3-day intervals.

Remote sensing has the potential to greatly improve our ability to measure components of the air-sea heat fluxes that are important forcing functions for the ocean and atmosphere. One of the most important air-sea coupling mechanisms is the sensible heat transfer at the air-sea interface. The air-sea sensible heat exchange is important in structuring the atmospheric marine boundary layer and modifying the available potential energy in the lower atmosphere. It can drive global atmospheric and ocean circulation and play an important role in global heat balance. Now accurate in situ measurement of air-sea sensible heat exchange is possible and airborne measurement can be achieved in the near future. The feasibility of daily space sensing of air-sea sensible heat flux with global coverage should be assessed.

The problem is that most remotely sensed oceanographic data available from space borne platforms are areal averaged surface estimates and inherently lack sufficient in-situ data for "sea truth" and validation. Another project goal is to develop and demonstrate improved algorithms, sensors and methods to analyze, merge and validate in-situ and remotely sensed oceanographic and meteorological data from drifting buoys and space borne sensors in an advanced and technology based demonstration. These validated, merged data can then be used to provide an environmental analysis capability and inputs for near surface values and forcing functions to improve regional and global scale atmospheric and oceanic circulation models.

This project would complement the existing NRL participation in the SERDP-funded project on Acoustic Monitoring of Global Ocean Climate. Both NRL and the University of Colorado Center for Astrodynamics Research (CCAR) are represented on the TOPEX/Poseidon and ERS-1 Science Teams. In addition, NRL is represented on the World Ocean Circulation Experiment (WOCE) Working Group on Numerical Modeling and the international Scientific Committee on Ocean Research (SCOR) Working Group on Acoustic Thermometry of Ocean Climate. NRL is one of five national centers selected for the collection and analysis of SeaWIFS color data and is represented on NASA's SeaWIFS Science Team and NOAA's Coast Watch Program.

7. Project Description:

This project addresses the following R&D objectives listed under Global Environmental Change in the SERDP Strategic Guidance: (objective 2) remote sensing capabilities in support of environmental change research and enhanced observation strategies and systems, (obj. 3) determine the impact of global ocean variability, (obj. 5) develop methods for analyzing and merging remotely sensed and in-situ data measurements, (obj. 6) develop numerical methods

to establish efficient environmental monitoring systems at regional and global scales, (obj. 7) develop enhanced ocean/atmospheric circulation models with the capability to forecast significant global environmental events at local and regional scales, (obj. 8) effects of weather system changes on water quality among other things, (obj. 9) understanding surface processes and ecosystems and their relationship to global environmental change. The effort also address a Grand Challenge Problem ("a global ocean prediction model") as defined in the Federal High Performance Computing Program (1989, Office of Science and Technology Policy). This program provides supercomputer time at no charge to DoD R&D projects and is a major source of computer time for this project.

The project components are: (1) eddy-resolving global and coastal models (obj. 6,7), (2) satellite measurements of oceanic and atmospheric parameters (obj. 2,5), (3) in-situ data for validation and assimilation (obj. 5), and (4) data assimilation techniques (obj. 5,6).

The ocean models are the NRL 1/8 degree eddy-resolving global model and the Princeton model for coastal applications. These will be run on supercomputers such as the NRL CM-5 under the DoD High Performance Computing Initiative, the Cray at NAVOCEANO and the SERDP funded Cray at the University of Alaska. Project members are already using the Alaska computer under the SERDP funded Acoustic Thermometry project. The models would run in pure simulation mode driven by atmospheric forcing (winds, heat fluxes, and moisture fluxes), validated against remotely sensed and in-situ data, and used to interpret and understand observed oceanic anomalies (obj. 2,3). The NRL model has exceptional dynamical modularity and can be used to include and exclude a wide variety of dynamical/physical processes. This and the high efficiency of the model (obj. 6) make it very effective at unraveling the dynamics of many observed oceanic phenomena. The models would also be used in observing system simulation studies (obj. 2) and to assimilate remotely sensed and in-situ data (obj. 5). Ocean models are essential for this as explained in the problem statement. Coupling of the global and coastal models is also planned.

A major aspect of the project would be the intensive examination and application of several types of remotely sensed data (altimeter, ocean color, IR, SSM/I, SAR, scatterometer) (obj. 2). NRL and CCAR have developed effective techniques for analyzing satellite altimeter data and assimilating it into ocean models (obj. 5). University of Rhode Island is developing a 12 hourly history of satellite IR SST's from 1981 to the present and has developed successful techniques for automated frontal analysis using the satellite IR data (obj. 2,5). NRL has developed effective techniques for assimilating frontal information into ocean models (obj. 6). Ocean color from SeaWIFS will be another valuable source of frontal information. In addition, NRL plans to use ocean color to investigate: (1) the role of bio-optical properties in the oceans heat content, (2) the role of incident short wave radiation on the upper ocean biological and optical properties, (3) the role of the ocean circulation and heat transport on bio-optical properties, and (4) the use of temporal variability in ocean color to monitor global carbon flux (obj. 2,9). Pollutant transport will be investigated in selected regions using the coastal model, ocean color and other satellite data (obj. 2,8).

Another aspect of this program is to determine and possibly quantify the ocean surface heat flux retrieval based on currently available sensor data, including AVHRR, SSM/I, IR, SAR and others. The sensor data will be used in conjunction with numerical model simulations and objectively analyzed synoptic fields. Airborne sensor measurements with in situ direct flux measurements from moored and drifting platforms will be made to calibrate, validate and refine the retrieval techniques for the space based sensors.

GOMAP Project Plans for the $900K of FY94 Funding

1. Hire Jean-Francois Cayula who is the world's leading expert on automated oceanic frontal analysis using satellite IR. His work is the first to clearly demonstrate the feasibility of doing this in a way that would be useful to the GOMAP system. Planned start 7/94
2. Demonstrate assimilation of IR frontal locations by a $1/8^0$ eddy-resolving model of the Pacific Ocean north of 20^0S.
3. Investigate the origin and dynamics of 5-year changes in sea surface height using satellite altimeter data from the Geosat-ERM, ERS-1 and TOPEX/Poseidon altimerty and simulations by $1/4^0$ NRL global ocean model.
4. Improve lagrangian characteristics of drifting buoys, complete thermistor chain development for heat flux evaluations and prepare 15 test buoys for evaluation.
5. Begin investigating the dynamics of the Agulhas retroflection using several versions of the NRL global ocean model, satellite altimetry, ocean color and IR data and existing in situ observations.

8. Expected Payoff:

This effort will result in increased ability to understand, monitor and predict global change, and synthesize and interpret satellite and in situ data. This includes a decade-long archived synthesis of global satellite and in situ data from the GOMAP system at 15km resolution and 3-day intervals. Other DoD and civilian applications include: tactical planning; input to ice, bio-physical and coastal models; ASW; optimum track ship routing; long range weather prediction; search and rescue; climate and El Nino monitoring; ocean resources (fisheries, seabed, structures); pollution and tracer tracking. Global observations of sensible heat transfer from space can benefit short range weather and marine prediction while improving our understanding towards climate change prediction on local and global scales. The development of retrieval algorithms would improve the estimate of this important exchange between the atmosphere and the ocean.

9. Milestones:

1.	Demonstrate assimilation of IR frontal locations by the ocean model.	12/94
2.	Review of existing data acquisition techniques.	08/95
3.	Investigate the dynamics of the Agulhas retroflection using the NRL global ocean model and satellite altimetry, IR, and the ocean color.	12/95
4.	In-situ measurement	06/96
5.	Validation of sensible heat retrievals	09/96
6.	Demonstrate the assimilation of ocean color frontal and turbidity data into the global and coastal models	09/96
7.	Demonstrate eddy-resolving global ocean monitoring using the 1/8 degree global model + satellite/in-situ data	09/96
8.	Enhance in situ measurement	09/97
9.	Investigate inter-basin exchanges in the path of the global ocean "conveyer-belt" circulation	09/97
10.	Compare measurements with simulation results	09/98
11.	Continuous global synthesis of satellite and in situ data 1985-97 using the 1/8 degree global ocean model with atmospheric forcing	09/98

12. Investigate the predictability of observed oceanic anomalies 09/98
13. Complete analysis of measurement results 09/98
14. Investigate the origin/dynamics of oceanic heat transport anomalies including the critical effects of eddies 09/99
15. Recommendation for advanced space sensor suite 09/99

10. Transition Plan:

The collaborating Naval Ocean Modeling and Prediction program has a 6.3 component designed to transition the ocean monitoring and prediction system to operational use at Fleet Numerical Oceanography Center in Monterey, CA. The NOAA Center for Ocean Analysis and Prediction, also in Monterey, works with FNOC to develop civilian applications of FNOC products. Discussions have been held with Ocean Routes, Inc. concerning a Cooperative Research and Development Agreement (CRADA) based on commercial exploitation of an eddy-resolving GOMAP system.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	900	4000	4000	4000	4000	3100	20000
DoD	3500	3000	3000	3000	3000	3000	18500
Total	4400	7000	7000	7000	7000	6100	38500

12. Performers:

NRL, University of Colorado, Drexel University, University of Washington, University of Rhode Island, Canadian National Water Research Institute

13. Principal Investigators:

Dr. Harley Hurlburt
NRL Code 7323
Stennis Space Center, MS 39529-5004
TEL: (601) 688-4626
FAX: (601) 688-4759

Dr. Simon Chang
NRL Code 7530
Monterey, CA 93943
TEL: (408) 656-4764
FAX: (408) 656-4769

Dr. Ken Ferer
NRL Code 7410
Stennis Space Center, MS 39529-5004

14. Keywords:

Global Ocean Variability, Ocean Modeling and Prediction, Global Ocean Observing System (GOOS), Satellite Remote Sensing, Data Assimilation, Air-sea Fluxes.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Comparison of CIRRIS 1A and UARS/ATMOS Databases

3. **Agency:** United States Air Force

4. **Laboratory:** Phillips Laboratory/GPOS

5. **Proposal ID:** #100

6. **Problem Statement:**

A major portion of the global changes research effort has been applied to fully understanding the processes leading to the observed depletion of stratospheric ozone. The early one dimensional photo-chemical models adequately described an 'average' stratosphere utilizing gas phase data but had problems at high latitude, particularly for the winter and spring simulations. These models evolved from one to two and three dimensions which include transport and atmospheric dynamics and include both more extensive accounting of the gas phase chemistry and under certain conditions, heterogeneous chemistry occurring on aerosols and polar stratospheric clouds (PSCs). These additions have significantly improved the simulation capability of these models especially during the breakup of the antarctic vortex during the austral spring. In order to properly observe these stratospheric photo-chemical changes NASA has launched a series of atmosphere observing satellites. These include ATMOS, SAGEII, LIMS, SAMS, TOMS, SBUV, and finally the most recent and extensive survey of stratospheric constituents,UARS. More detailed examination of the satellite data from TOMS and SAGE along with observations from ground based Dobson instruments clearly shows a 0.3% drop per year in ozone concentrations from 1980 to 1990 which can not be explained using gas phase chemistry alone. There is presently speculation that aerosols in the lower stratosphere at mid to low latitudes create an environment where significant heterogeneous chemistry exists. The launch of UARS in September 1991, three months after the June eruption of Mount Pinatubo and the ATMOS ATLAS 1 flight in March 1992 during peak loading of the stratosphere by Pinatubo aerosols provide a special opportunity to study the effect of a large injection of sulfurous aerosols into the mid-latitude stratosphere. An essential data set missing from the UARS database needed to fully understand the effect of these aerosols on important heterogeneous processes such as, $N_2O_5 + H_2O$ ------> $2HNO_3$, is a set of pre-Pinatubo eruption observations. Fortunately, there exists a database from the Air Force's CIRRIS 1A program, a cryogenically cooled infrared interferometer flown aboard the space shuttle in April 1991, just 2 months prior to the Mount Pinatubo eruption. It is the analysis of the stratospheric data contained in this CIRRIS 1A database and its inter-comparison with NASA's UARS, ATMOS, and SAGE II databases that is proposed here.

7. **Project Description:**

The CIRRIS 1A database includes simultaneous spectral observations from 2.5 to 25 μm (400 to 4000 cm^{-1}), tangent height scans from the Earth's surface to 260 km, latitude coverage from 70 degrees north to 70 degrees south for both day and night conditions. The quality of the data is excellent with the best scans possessing a signal to noise of 5000 to 1 or higher. First a survey of the CIRRIS 1A database will be performed in order to extract a subset of data which is

relevant to stratospheric and upper thermospheric chemistry. This subset will be used to determine which species identification, column density and concentration profiles can be retrieved. From preliminary investigations, significant information about the following atmospheric species is most likely to be available, NO, NO_2, N_2O, N_2O_5, HNO_3, $ClONO_2$, CFC-11 and CFC-12. The CFC data will be very useful for the global changes long lived species database while the NO_y data gives the unique opportunity to provide the baseline effect of background level aerosols on the de-nitrification of the lower stratosphere. The second phase analysis will utilize the simultaneous constituent concentration profile retrieval algorithm developed for the Air Force's CIRRIS and MSX programs to obtain concentration profiles for the above species at a variety of latitudes and times of day. The NO and NO_2 concentration profiles can then be compared to the N_2O_5 and HNO_3 profiles to determine the baseline NO_y catalytic cycle. This will be accomplished using either simple analysis techniques or if necessary utilizing two dimensional photochemical modeling. The third phase will be an inter-comparison between the CIRRIS data extracted and the appropriate UARS data. If the surface reaction probability for the reaction $N_2O_5 + H_2O \longrightarrow 2HNO_3$ is as high as 0.14 then a significant difference in NO, NO_2, N_2O_5, and HNO_3 concentrations should be readily observable between the pre-Pinatubo eruption CIRRIS 1A observations and the post-Pinatubo eruption UARS observations. This analysis along with estimates of aerosol concentrations during the two observations provide an excellent test of the effects of sulfate aerosols on stratospheric chemistry. The final phase of this study will be to simulate the above results with a two dimensional photo-chemical model and subsequently improve these models with the appropriate modifications.

Hofmann and Solomon reviewing the literature and utilizing NIMBUS 7 and LIMS data along with ground station and balloon data of a variety of stratospheric species have made a convincing argument that the sulfate aerosols injected into the stratosphere from the eruption of El Chichón in Mexico in March and April of 1982 had a significant impact on the ozone levels at mid-latitudes. They argue that transport alone cannot account for the ozone reduction (about 10%) observed several months after the eruption and that heterogeneous chemistry upon the resulting sulfuric acid aerosols has a major impact.

Considine compared their two dimensional photo-chemical model with and without the heterogeneous reaction $N_2O_5 + H_2O \longrightarrow 2HNO_3$ included, with both LIMS and in-situ measurements made by NASA's ER2 aircraft. The study examined background zonal aerosol levels in the stratosphere. Their results indicated that the HNO_3 levels measured by LIMS are modeled more closely when the above heterogeneous reaction is included in the modeling, while the NO_2 concentrations measured using the in situ measurements are modeled more accurately if only gas phase reactions are included. They conclude by indicating that further measurements of lower stratospheric constituents and comparisons with model calculations are necessary to resolve these inconsistencies.

Finally, Koike measured column densities of NO_2 and O_3 using a solar scattering spectrometer at Moshiri Observatory starting in April 1991 and continuing through the Mount Pinatubo eruption. They observed significant reductions (15%-50%) in NO_2 column densities that corresponded well with the transport and subsequent dispersal of mid-latitude aerosols originating from the Mount Pinatubo volcano. They concluded that the observed NO_2 decrease is likely to be due to the heterogeneous reactions upon the volcanic aerosols.

8. Expected Payoff:

Clearly, the effect of aerosols on both stratospheric chemistry and global warming is of significant concern to the global changes research community. The mid-latitude ozone loss over the last decade cannot be explained by gas phase chemistry alone and the heterogeneous chemistry permitted by the presence of aerosols is not well understood. This study will provide one of the few clear comparisons of stratospheric chemistry under conditions of background and aerosol rich environments.

The DoD can benefit significantly by this study in two ways. First, by utilizing the understanding of aerosols gained to examine the future effects of the exhaust of high altitude aircraft and secondly by gaining significant information on the changes in infrared radiation intensity in the atmospheric window regions used for surveillance and target detection. An additional benefit can be obtained by the comparison and validation of Air Force and NASA concentration profile retrieval algorithms.

9. Milestones:

1.	Survey of CIRRIS data base	04/95
2.	Temperature/Species profile retrieval	09/95
3.	Comparison with UARS/ATMOS data	09/96
4.	Two-dimensional photo-chemical modeling	09/96

10. Transition Plan:

All results of this study will be transitioned to the global changes database. In addition, the tools and knowledge gained in this study will be utilized in the analysis of the future MSX (Mid-course Space experiment) database.

11. Funding: ($K)

	FY94	FY95	TOTAL
SERDP	395	395	790

12. Performers:

The principal performers of this study are Steven M. Miller of the U.S. Air Force Phillips Laboratory and Curtis P. Rinsland of the National Aeronautic and Space Administration along with appropriately chosen contractors.

13. Principal Investigator:

Steven M. Miller
PL/GPOS (Air Force Phillips Laboratory)
29 Randolph Road
Hanscom AFB, MA 01731-3010
PH: (617) 377-2807; FAX (617) 377-8900; EMAIL miller@gl9000.plh.af.mil

14. Keywords:

Aerosols, Heterogeneous, Chemistry, CIRRIS 1A, UARS, ATMOS

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Environmental Requirements for Cloud Analysis

3. **Agency:** Air Force

4. **Laboratory:** Phillips Laboratory

5. **Proposal ID:** #098

6. **Problem Statement:**

This proposal is for the advanced development and demonstration of technology for retrieving and combining the environmental information, in particular cloud data, routinely provided by various remote sensing satellite systems into a single, optimal multi-parameter cloud specification methodology applicable on a global scale and available in a continuously updated real-time and archived format. The U.S. Global Climate Change Research Program has identified clouds as the environmental variable having the greatest impact on climate change processes and having the highest priority for improved specification. Both DoD and civilian researchers have identified more complete and more accurate global cloud specification as the primary need in improving the present primitive state of cloud prediction technology. Additionally, the Defense Modeling and Simulation Office has emphasized the need for comprehensive and detailed cloud parameter specification in its Environmental Effect-Distributed Interactive Simulation program.

The performance of modern strategic space-based infrared detection systems (the Defense Support Program) and tactical aerial targeting systems (for example the Infrared Search and Track system) are materially enhanced by timely global cloud analyses which specify the radiative and microphysical properties of cloud. Since the atmospheric transmission path is an integral component of an overall sensor system, cloud induced changes to atmospheric attenuation characteristics can severely compromise the effectiveness of such electro-optical sensors. Cloud parameters analyzed based on the Support of Environmental Requirements for Cloud Analysis and Archive (SERCAA) - Phase I algorithms primarily support initialization of cloud forecast models. Phase II cloud parameters including optical thickness, cloud phase, particle size information, emissivity, and cloud bases, in addition to cloud environment parameters including total condensed water content and precipitation rate, directly address the data requirements for characterization of electro-optical impacts on weapons sensor and surveillance systems. The availability of such cloud and cloud environment data will not only enhance the utility of present surveillance and targeting systems, but will also guide the development of the next generation systems.

Current cloud analysis approaches underutilize available satellite remote sensing data and lack the potential to fully exploit the next generation of satellite sensors. The number and type of satellite-borne environmental sensors is large and growing. For example, onboard the two U.S. polar orbiting satellite platforms, DMSP and NOAA, there are two different multispectral imagers, four different microwave sounders, and a multi-channel infrared sounder. The planned Earth Observing System (EOS) will add an even greater number of sensor suites. The amount and accuracy of environmental information obtainable by passive remote sensing is dependent upon the number of quasi-independent radiance measurements made. The spectral diversity of

satellite sensors is great, providing the potential to infer significant high quality cloud information. Current satellite cloud specification technology does not combine the cloud information measured by diverse sensors. Differences in sensor fields-of-view, bandwidths, viewing geometries and times of measurement are all factors that must be resolved in a unified retrieval technology to optimally exploit the total information content of diverse multispectral satellite sensors. Such technology has been developed and demonstrated in SERCAA - Phase I for the elementary cloud parameter, cloud amount. The retrieval, optimal interpolation, and analysis integration technologies for the more analytical cloud properties (radiative and microphysical), which are recognized as having first order impacts on environment and climate, are provided for by SERCAA - Phase II.

This proposed effort constitutes the completion of the applied research and technology demonstration of the advanced satellite-based global cloud specification methodology begun with SERDP FY92 support. That project, SERCAA - Phase I, carried out during the 18-month period Nov 92 - Apr 94 with Defense Support Project Office sponsorship, has resulted in advanced development, validation, and demonstration (DV&D) of multisatellite multi-spectral algorithms for the specification of cloud spatial characteristics (cloud presence, amount, height, and cloud type) anywhere on Earth. These algorithms are being used as specification for the next generation real-time global cloud analysis system being procured and implemented to support DoD operational and other national needs. This proposed completion is summarized as DV&D of multisatellite multi-sensor algorithms for the specification globally of cloud radiative (emissivity and optical thickness), microphysical (particle size and phase), and environment parameters (temperature, water vapor and condensed water content, and precipitation rate) and for the prototyping of a continuously updating archive of all SERCAA - Phase I and II global cloud information.

7. Project Description:

The identified SERCAA - Phase II program objective is to demonstrate the integrated analysis methodology developed for cloud amount for the complete set of cloud and cloud environment parameters obtainable from comprehensive analyses of multisatellite data and to prototype the archive of these integrated products.

Exploitation of available satellite sensor resources on both polar and geosynchronous platforms for cloud characterization requires a capability to assimilate and process diverse data streams. Sensor data differ in spatial, spectral, and temporal resolutions. In order to accommodate a variety of operational sources an optimizing approach is required. The integration is performed on analyses, not on raw radiance data, and the integration process is engineered to ensure that the strongest assets of the diverse observations of each particular cloud parameter are appropriately contained in the final optimal analysis.

A straightforward approach for the fusion of data from multiple sensors/platforms that exploits the strengths of the best data available can be based on the analog of numerical weather prediction (NWP) model observational data assimilation. NWP data assimilation techniques provide an objective analysis of the state of the atmosphere from conventional and satellite observing systems while accounting for the magnitude and correlation structure, if any, of the errors of each. The SERCAA data integration approach recognizes that certain environmental elements, such as clouds, are not continuous in space or time, and that simple methods of interpolation or weighing will yield unrealistic fields. Rather than attempting to blend the raw data provided by various satellite sensors, the SERCAA integration is performed on the

individual cloud parameter analyses from the different satellites sensors. This allows for maximum exploitation of each sensor's information content. The integration process will include decision algorithms based upon age and quality of analysis products, and will account for the strengths of each particular data source in specifying a particular cloud attribute. Where timely analysis data are not available, short-term prognostic fields may be useful inputs to the decision algorithms in the applied integration process. Information integration also includes the effective use of sounder sensor data to enhance the comprehensiveness of the final cloud and cloud environment analysis.

The establishment of the prototype of an easily used and widely accessible archive of the integrated cloud analysis products is planned. This archive will be global in scope, with areal resolution of 25 x 25 km^2 and with hourly temporal resolution, and will be of the quality required for global change research.

This SERCAA - Phase II effort will provide an all-parameter integration of multiple-source cloud analyses. The focused objective of Phase II is to DV&D the fused analyses for the complete set of cloud parameters obtainable from the multiple satellite sources and to provide a prototype archive of these products. Phase II is therefore an enhancement to Phase I of the SERCAA project.

The tasks are: 1) develop multi-spectral algorithms for enhanced set of cloud parameters: emissivity, optical thicknesses, mode radius, cloud base, cloud particle phase, 2) validate the individual algorithms, 3) apply the analysis integration approach developed in SERCAA-Phase I to these parameters, 4) demonstrate the operation of and validate the integrated analysis technology, 5) specify cloud environment using collocated satellite sounder (infrared and microwave) data, 6) establish a prototype archive of spatial and enhanced cloud parameter sets.

The risks center around resources vis-a-vis technology. The experience of DV&D of spatial algorithms during SERCAA-Phase I has reduced the level of risk involved in individual detection and integration algorithms. On the other hand, the same experience has demonstrated that high-end data processing and image manipulation resources are critical especially in the validation effort and that the insurance of the availability of such equipment, along with the highly trained research manpower to employ these data devices, is a perceived risk in the prevailing environment of decreasing support budgets and manning reductions. The increased reliance on contracted capabilities is the risk mitigation strategy. The satellite data acquisition, handling, and analysis computer resources and the research team employed in the successful execution of SERCAA-Phase I presently remain intact and are the lowest-risk option for the accomplishment of SERCAA-Phase II.

8. Expected Payoff:

The SERCAA-Phase II provision of cloud optical, microphysical and cloud environment parameters to this global cloud analysis methodology is a paramount enhancement of the U. S. Global Climate Change Research program. The payoff to developing cloud prediction technology is also first-order since accurate and timely cloud analysis is the presently unavailable requirement. The expected operational payoff from the integrated global cloud specification provided by this DV&D project is the more effective utilization of space based surveillance assets. More generally, the integrated analysis technology can be applied to many multi-source remotely sensed environmental variables. Beneficiaries of the superior cloud products contained

in the archive will be the program of the Defense Modeling and Simulation Office and the global environmental change research community.

9. Milestones:

1. Demonstration of full parameter integration	12/94
2. Limited area archive operation	04/95
3. Full parameter all-satellite integration	01/96
4. Global archive operation	08/96

10. Transition Plan:

An immediate benefit is the specification of the size requirements, in hardware and software terms, of the technical transition task of this capability to exploit the total cloud information contained in all available satellites. The technical transition of this specification is being executed by the Air Force Space and Missile Center for the Air Weather Service.

The enhanced cloud parameter and analysis integration algorithms are contained as elements of the pre-planned product improvement (P^3I) of the USAF/XOW Cloud Detection and Forecast System (CDFS)-II procurement. The location for implementation of CDFS II and its P^3I elements is the central satellite data and weather analysis site, presently at Offutt AFB, NE. The detailed transition plan is contained in the Operational Requirements Document for CDFS II, USAF ORD 005-92-I/II/III, 3 SEP 93.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP	1470	0	800	500	300	1600
6.2 (AFMC)	230	350	250	250	250	750
Total	1700	350	1050	1000	850	2900

12. Performers:

Organizations that will participate in this work include the Department of Defense, Phillips Laboratory - Geophysics Directorate (PL/GP), Atmospheric Sciences Division, Satellite Meteorology Branch (GPAS), Hanscom AFB, MA and the Department of Commerce - National Oceanographic and Atmospheric Administration, National Climatic Data Center (NOAA/NCDC).

Demonstrated understanding of the complexity of multi-satellite data integration and a plan-of-attack for applying various techniques to achieve accurate, current and maximally informative analyses of a number of environmental variables including clouds, have been exhibited by Atmospheric and Environmental Research, Inc., Cambridge, MA. The Broad Agency Announcement of PL/GP is applicable for such industry involvement.

The need for and the payoff from information integration technology for multiple satellite sources has long been recognized. The remote specification of atmospheric parameters in addition to clouds specifically addressed in SERCAA, such as water vapor, turbidity, and temperature, and also of surface characteristics such as saturation and vegetative state can all benefit from the multi-source analysis integration technology to be demonstrated in the SERCAA - Phase II project. The ground work has begun from expanding the satellite data integration technology to provide marketable environmental data and analysis products. The SERCAA algorithms are considered a viable item for the government/industry Cooperative Research and Development Agreement (CRADA) initiative.

13. Principal Investigator:

Dr. J. William Snow
PL/GPAS
Phillips Laboratory - Geophysics Directorate
Hanscom AFB, MA 01731
TEL: (617) 377-3496, 3497
FAX: (617) 377-2984, 8892

14. Keywords:

Satellite remote sensing, satellite retrieval algorithms, satellite cloud detection, cloud radiative properties, data fusion, analysis integration,

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Atmospheric Remote Sensing and Assessment

3. **Agency:** DOE

4. **Laboratory:** DOE: Sandia National Laboratories

5. **Proposal ID:** #470

6. **Problem Statement:**

This research proposal is a continuation of the DOE-DoD SERDP program to develop improved measurements and understanding of the Earth's atmosphere and its response to global change. In the spirit of SERDP, we are drawing heavily on DoD and DOE defense capabilities to "develop innovative technologies to measure stratospheric ozone levels and the radiatively important trace gases...to understand their effects on climate systems." Both DOE and DoD need improved measurements of trace gases, radiative fluxes, cloud properties, and water-vapor profiles. These are critical to understanding three key global change issues: (1) the role of radiation-cloud interactions on the earth's radiation budget; (2) the evolution and fate of ozone in the middle atmosphere; and, (3) the couple effect of increases in greenhouse gases and ozone depletion on climate change and the potential for early detection of global change in the middle atmosphere. In addition, these measurements are of high priority to the DoD for improved atmospheric and near space weather forecasting, for predicting infrared backgrounds for surveillance weapon sensor systems and for characterizing ionosphere effects on communications and satellite drag and missile reentry dynamics.

Radiation-cloud interactions are the dominant uncertainty in current atmospheric climate models. Reduction of this uncertainty is the top scientific priority of the U.S. Global Change Research Program and the DOE's Atmospheric Radiation Measurement (ARM) program. To date, the ARM program has emphasized ground-based measurements to test and refine models of these interactions. However, major studies by JASON, DOE and NASA have highlighted the fact that certain critical information is better attained through sustained airborne measurements. This program addresses these needs by developing improved airborne measurements of (1)radiative fluxes at the top-of-the-troposphere; (2)radiative heating within the troposphere; (3)cloud top and multi-layer cloud properties; (4)upper tropospheric water vapor profiles; and (5) calibration of satellite-derived fluxes.

Middle atmospheric ozone depletion is among the most important global change problems. The discovery of the dramatic ozone depletion occurring in the Antarctic spring "ozone hole" has verified that chlorine catalyzed ozone destruction (resulting from anthropogenic activities) does in fact occur. However, we currently have no idea of the ramifications of this local ozone depletion for global ozone change. Current models are not successful in completely reproducing the present global ozone depletion. Thus, there is little confidence in future trend predictions. However, these model predictions are urgently needed in order to develop effective public policy concerning such important issues as CFC emission ceilings. Currently, model improvements are severely hampered by the scarcity of measurements of constituents required to completely describe important ozone photochemical processes. In addition, it is becoming increasingly clear

that the various atmospheric regions and their global change issues are linked through complex coupling mechanisms, and it is impossible to effectively study any one region in isolation from the others. For example, CFC's, which are known to catalytically destroy ozone, are also important greenhouse gases and contribute to global warming. Also, middle atmospheric ozone distribution drives the middle atmospheric circulation system which, in turn, acts as steering currents for surface weather systems. Thus, middle atmospheric ozone depletion could modify the climate at the surface. Important signatures of increasing greenhouse gases are present above the troposphere. These signatures are more easily discernible above natural variability than in the troposphere and may provide early indications of global warming.

The status of the ARSAP tasks was reported to SERDP Executive Director in the Progress Report of 10 September 1993.

7. Project Description:

The DoD and DOE have made substantial investments in global remote sensing of the atmosphere. This includes sensor development and theoretical modeling to interpret the observations by extending local process physics and chemistry to global scales. These programs have been oriented toward agency mission requirements for defense applications. This SERDP program enhances and focuses the combined experimental and theoretical activities toward the atmospheric global change problem and the development of an improved predictive capability. This research has three major components: 1) measurement and monitoring, 2) unique database systems for evaluation of global change, and 3) photochemical, dynamical, radiative theory and modeling programs.

The measurement and monitoring component includes eight on-going space flights as well as ground-based sensors to measure most of the important neutral and ionized components of the middle and upper atmosphere. Stratospheric ozone depletion processes are measured by the Millimeter-wave Atmospheric Sounder (MAS) which flies on the NASA ATLAS Series Spacelab missions. In its two previous flights, MAS surveyed the global structure of the stratosphere including ClO, the key element in chlorine catalyzed ozone depletion. An improved SERDP-funded ClO sensor will fly on ATLAS-3. The planned yearly MAS flights on ATLAS will monitor the role of chlorine in stratospheric evolution through the next century. ATLAS-3 will also include the Middle Atmosphere High Resolution Spectrograph (MAHRSI) measurement of stratospheric OH and NO, completing for the first time the basic set of constituent measurements needed to describe ozone photochemistry. MAHRSI joined the ATLAS series as a result of SERDP. The Polar Ozone and Aerosol Monitor (POAM) and its planned follow-ons monitor the stratosphere. Launched on SPOT-3 in September 1993, POAM has already documented the annual Antarctic ozone hole in unprecedented detail. In addition, SERDP has made it possible to build a geophysical database management system for POAM and to begin fabrication of its follow-on which will monitor the mid-latitude stratosphere. The Remote Atmospheric and Ionospheric Detection System (RAIDS), High Resolution Airglow and Auroral Spectrograph (HIRAAS) and (GIMI) extend global monitoring into the mesosphere, thermosphere and ionosphere. These sensors utilize UV spectroscopy to monitor major species composition and temperature, and trace chemical components which respond to global change in the lower atmosphere. These SERDP sensors use the Space Test Program for their launch opportunities and are prototypes for operational monitors.

Another measurement thrust attacks the major uncertainty in global warming predictions, i.e. radiation-cloud interactions. To achieve the required improvement in radiation and cloud

measurements, we are developing both new instruments and new measurement techniques. These are geared toward commercial unmanned aerospace vehicles(UAVs) to provide the necessary endurance and altitude. We are currently developing four instruments: a net flux radiometer (HONER) that uses a novel optical differencing technique, a calibrated, multichannel, wide field of view cloud radiometer (MPIR), a cloud detection lidar (CDL), and a UAV version of a ground-based ARM interferometer (UAV-AERI). In addition, we are taking the first major steps in utilizing UAVs for climate measurements. We have integrated an initial radiometric payload into a UAV and are in the process of using a single UAV to demonstrate clear sky flux profiling and will shortly use two UAVs to demonstrate simultaneous flux profiling for cloudy skies. This proposed continuation leverages these efforts in three ways. First, it provides for the flight testing and calibration-validation of the new instruments; Second, it fills two key remaining measurement gaps: development of a UAV-compatible differential absorption lidar (DIAL) for profiling upper tropospheric water vapor; and, development of UAV-compatible in-situ instruments for supplementing the remote measurements. Third, it will extend the UAV measurement techniques to high altitude, by providing long range flights for characterizing large scale radiative and convective phenomena. Due to technology we originally developed for defense applications, there is minimal risk in extending these to UAV-compatible instruments. The resulting measurements strongly complement the ground-based ARM measurements and use UAV technology from DoD and NASA.

The second component of this research effort, data systems, supports the measurement effort. State-of-the-art data base systems are being developed which allow the data from remote sensing missions to be readily accessed and displayed. Data from the DoD sensors will be fully integrated into, and accessible through the NRL/DoD Backgrounds Data Center (BDC). The BDC will be networked with DOE data systems. The DOE data system has been developed to support ARM/CART data and augments the Carbon Dioxide Information Analysis Center at Oak Ridge National Laboratory. This facility is also part of NASA's data system and provides an easy accessibility to the scientific community through use of Global Climate Data Information System (GCDIS) approved procedures.

The third component of this research effort is a theoretical modeling program. NRL currently has an operational l-dimensional photochemical model of the middle atmosphere, and a 2-dimensional photochemical/dynamical model which became operational in FY 93. A 3-dimensional capability is also under development. This includes coupling between the lower, middle, and upper atmosphere, including the momentum transport and deposition in the upper atmosphere. Models of the solar forcing of the atmosphere are also being developed to study natural variability. DOE's ARM project has a similar modeling program for the troposphere. We plan to use the models in a synergistic fashion with the measurements. That is, the measurements will be used to test various model parameterizations and, thereby improve these parameterizations. In turn, the models will be used to interpret the measurements. An important component of both the DoD and DOE model development programs is the utilization of high speed computing techniques and resources.

All three components are closely tied to other national programs to study global climate change currently in place at NASA and other Committee on Earth and Environmental Sciences (CEES) agencies, and is either complementary or, in the case of NASA, fully integrated.

8. Expected Payoff:

The radiation, water vapor, and cloud measurement capabilities will be an important complement to the ARM program and serve as the basis for a future ARM-UAV program to be funded by DOE. This will be a unique capability for long endurance radiative heating measurements up through the tropical tropopause (20 km) and will allow 'indirect calibration' of satellite data, thereby greatly leveraging the use of existing weather satellites. These improvements can also provide the DoD with enhanced weather data, with redundancy in the case of satellite loss during critical operations, and provide improved infrared backgrounds for weapon system sensors. Representatives of both the Defense Meteorological Satellite Program (DMSP) and of NOAA have expressed interest in several of the instruments for weather satellite applications. The UAV demonstrations will be a key step in establishing these platforms as a "better, faster, cheaper" complement to satellite measurements.

The measurements of the upper atmosphere fill an urgent need for space-based atmospheric measurements during the 1995-2000 time frame. The NASA Upper Atmospheric Research Satellite (UARS) was launched in September 1991 and has a projected lifetime of 5-7 years and the Earth Observing System (EOS) atmospheric chemistry missions are scheduled for after the turn of the century. Thus, there is a gap which will be filled by this program during which policy decisions regarding global warming and CFCs must be assessed. Further, a continuation of this program complements the capabilities and global coverage of EOS allowing an uninterrupted series of measurements of the Sun/Earth/atmosphere system for two decades.

A significant benefit to this research activity is the cost savings realized by utilizing existing DoD and DOE observational and theoretical capabilities. Especially important is the leveraged costs of launching sensors into orbit. Existing data centers (BDC and GCDIS) will be used for data archiving and management.

9. Milestones:

1.	First space-based observations (ATLAS-2)	03/92
2.	Space flight of DoD POAM	09/93
3.	Fly clear sky mission/initial radiometric payload	03/94
4.	Conduct 2 UAV simultaneous flux profiling	09/94
5.	3D dynamical/photochemical model incorporating gravity wave orography and climatology	09/94
6.	Shuttle flight of three atmospheric sensors (ATLAS3)	10/94
7.	Conduct mid-latitude ozone mission	10/94
8.	Long endurance mission/CDL and HONER test	06/95
9.	Launch of ARGOS satellite with atmospheric sensors	08/95
10.	Tropical Pacific mission/MPIR test	02/96
11.	Launch of POAM follow-on	03/96
12.	Ocean margins mission/AERI test	11/96
13.	Test flight of DIAL and in-situ packages	06/97
14.	Space flight of DMSP upper atm./ionosphere sensors	11/97
15.	Complete analysis and transition of operation to DoD and DOE.	09/98

10. Transition Plan:

DOE will begin funding the ARM-UAV program in FY95 and will ramp up funding so that when SERDP development is complete in FY98, DOE will be funding the full cost of operations. In addition to this primary transition path, we will work with NOAA and DMSP to explore transitioning instruments to satellites. All data will be available through the DoD BDC at NRL and the GCDIS center at Oak Ridge. At least part of the DoD program will undergo transition to the DMSP in the form of upper atmospheric weather monitors. Data from this and other activities can be used to provide climate data for long term atmospheric change.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
DoD SERDP	8300	11200	6000	3100	1500	645	30745
DOE SERDP	25000	13500	12800	6000	2000	855	60155
Total SERDP	33300	24700	18800	9100	3500	1500	90900
DOE Non-SERDP	40000	48000	57000	69000	69000	69000	352000
DoD Non-SERDP*	10500	6300	4000	3900	3600	3500	31800

* Not including launch and data center costs (more than $15M/yr)

12. Performers:

Work will be conducted in-house at NRL, Sandia, Brookhaven, Los Alamos, Lawrence Livermore National Labs and Pacific Northwest Lab. University participants include Penn State, Johns Hopkins, Wisconsin, North Carolina State, Harvard, Maryland, Colorado, Colorado State, California at San Diego, Oklahoma, and Alaska. ARM research is also underway with grants from DOE to scientists at NASA Centers and with cooperative arrangements with NSF and NCAR. Industry participants include Computational Physics Inc, General Atomics, Aurora Flight Services, Thermoelectron Technologies Corp., Research Support Instmts., Millitech Corp., ARTEP, SFA, ATC.

13. Principal Investigators:

Dr. Schwartz
Code 7203
NRL
Washington, D.C. 20375
Phone: (202) 767-2351
FAX: (202) 404-7453

John Vitko
Sandia National Laboratory
MS9056
P.O. Box 969
Livermore, CA 94550
Phone: (510) 294-2820
FAX: (510) 294-2276

14. Keywords:

Global change, ozone, greenhouse, atmospheric remote sensing, global warming, radiation budget

SERDP FY94 Proposal

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Acoustic Monitoring of Global Ocean Climate

3. **Agency:** Advanced Research Projects Agency

4. **Laboratory:** Scripps Institution of Oceanography

5. **Proposal ID:** #286

6. **Problem Statement:**

Conduct a research program to measure and analyze changes in global ocean temperature to advance our understanding of short and long-term ocean variability and its relation to climate trends. The oceans play a key, but still poorly understood, role in the most important processes contributing to climatic changes such as heat and carbon dioxide storage. The main goal of this proposed research is to measure directly global ocean temperature trends using innovative underwater acoustic technologies, based on the fact that the speed of sound in water is proportional to temperature. A further goal is to develop an ocean-atmosphere modeling capability and supporting database to permit skilled forecasts of significant global environmental changes, which are of major impact in global change and climate prediction. Issues are (1) resolving the complex acoustic signal structure in order to track long term trends along specific acoustic paths, and (2) extracting the long-term trends from the background natural variability of the oceanic temperature field. Methods will be developed to incorporate these measurements into climate prediction models, and to merge them with satellite temperature and altimetry data acquired in other research programs. Enhanced ocean-atmospheric circulation models with the capacity to forecast significant global environmental events will be developed. An adjunct effort is the development of predictive stochastic models for evaluating the efficiency of specific realizations of large-scale, ocean, environmental monitoring systems.

The currently funded SERDP program initiated studies and demonstration technology developments to establish the feasibility of monitoring global ocean environmental change. Phase 2 will address: 1) crucial ocean-basin-specific geoacoustics issues in the Indian, South and North Atlantic and Arctic oceans; 2) validate new methods for integrating acoustic thermometry data with other synoptic sensor data into highly improved global ocean-atmospheric models; 3) extend the network of international collaboration and funded participation in the development of the global ocean acoustic network.

Background: Since ocean temperature is a key indicator of global climate change, accurate temperature measurements, spanning the world's ocean basins and sampled over a long period, are essential to complement atmospheric measurements of global climate trends. The capability to make synoptic temperature estimates derived directly from acoustic travel time measurements was demonstrated in the 1991 Heard Island Feasibility Test where acoustic signals were transmitted from a location in the Southern Indian Ocean to 14 receiver stations, manned by nine international scientific teams, in the Atlantic, Indian, and Pacific oceans. The test demonstrated that acoustic signals of moderate intensity can be received over global paths with sufficient signal to noise ratios to measure propagation time and spatial variability.

7. Project Description:

Status: The Acoustic Monitoring of Global Ocean Climate program was initially approved by the SERDP Council and the Scientific Advisory Board (SAB) as a Phase I program with the Congress providing initial funding in the Supplemental FY92 legislation. The SAB noted that; "This ambitious thirty-month proof of concept experiment is a follow-on to the successful three-week long, 'Heard Island' hypothesis testing experiment. Excellent scientists have been associated with this experiment and peer review protocols are used by its management. The ....broad international participation makes technical, economic, and political sense." ARPA competitively selected two university/industry teams for funding. In FY93, the SERDP Council and Congress continued the program.

The FY94 SERDP strategic guidance requires that Global Environmental Change programs be integrated with and specifically identified as "Contributory" programs in the U.S. Global Change Research program (USGCRP). The highest priority near-term scientific and policy-related issue for USGCRP is whether, and to what extent, human activities are changing, or will change, the global climate system. The goals of the Acoustic Monitoring of Global Ocean Climate program specifically address these issues.

Approach: The initial approach is to deploy acoustic sources near the deep sound channel (800-1000 m) and periodically transmit encoded signals of 20-minute duration at 70 Hz with 20 msec or better timing accuracy. Deep sources direct maximum signal power into the long-range horizontal paths, providing good signal to noise ratios at long range. These sources will require state of the art manufacturing techniques to develop the specified 70 Hz acoustic devices. Both vertical and horizontal arrays will be used to resolve acoustic arrival structures. The Phase 1 program uses the Navy's Integrated Undersea Surveillance System receiver assets and deploys newly developed vertical line arrays (VLA) at strategic points across the Pacific. Moored on the sea floor, each VLA contains 40 hydrophones and advanced signal collection, timing, and processing modules.

In a complementary technology development, the Woods Hole consortium under the direction of Dr. John L. Spiesberger, is developing a unique surface suspended, "drifting" acoustic receiver (SSAR). Through innovative use of satellite telemetry and global positioning system support, these drifting receivers will independently receive acoustic signals, fix their own position, calculate the acoustic path and process received acoustic data onboard; and then transmit all these data to a shore-based center via satellite link. Drifting receivers will push the state of the art in acoustic measurements and will provide the world oceanographic community with a much needed collection instrument. Twelve SSAR receivers will be built and deployed during Phase 1 to complement the fixed receivers in locations that best utilize the SSAR's mobility features. The SSARs will also be used extensively in the global network.

The Phase 2 follow-on program will design, install and operate a global network, incorporating cost effective source and receiver configurations based on experience from the present experiment, improved source/receiver/data handling technical designs and the geo-acoustics of the ocean basins being monitored. This is a vital extension to the current network and a key element to transition the program to NOAA for long term data collection and analysis. While Phase 1 will provide insights into preliminary options for long term acoustic monitoring, Phase 2 focuses on the continued sustainability of a global network. Operating such a powerful network over decades is a major technical challenge. Among the relevant Phase 2 objectives are testing and evaluating new source technology to achieve low cost, reliable production and

operating goals, gaining data on the circulation patterns of different ocean basins, and obtaining a deeper understanding of physical acoustics and propagation conditions globally. Phase 2 will also result in a cohesive global effort by international oceanographic researchers in the quest to understand the ocean and ultimately climate variability which is the intent of the USGCRP.

8. Expected Payoff:

This effort will directly benefit NOAA, U. S. Navy's oceanographic programs, and the world ocean research community by providing methods to measure and analyze ocean variability at large scales which is the key to global climate change issues.

- The emerging science of acoustic thermometry and the anticipated global network of sources will enable broad ocean climate variability research by the international oceanographic community, since the signal will be available to any country wishing to participate with their own acoustic receiver assets. The emerging global network will provide new techniques and opportunities for understanding ocean variability.

- Advances in methods for merging acoustic thermometry data with existing remote sensing (satellite) ocean data bases will en-able research where horizontal and depth resolution are key variables.

- Development and application of coupled ocean/atmospheric modeling and prediction systems will lead to such practical applications as better prediction of "El Nino" effects throughout the Pacific with recommendations on minimizing the economic impact.

- Advances in low frequency sources manufacturing technologies will provide the cost reduction, reliability and system performance needed for long-term ocean data collection programs. The technology advances are pivotal to establishing the long term network reliability in an internationally operated network.

- SSAR receivers and small recording-array technologies offer promise of a low cost method for long-term studies of ocean climate variability, ocean geophysics, monitoring of natural and man-made seismics and environmental monitoring, e.g., pollution tracking. Again, the advance of these technologies provides a principal basis for leveraging US technical leadership in long term monitoring.

- The results of comprehensive marine mammal monitoring will provide benchmark scientific data never before available on the impacts of low frequency sound on marine mammal behavior,to aid in setting better, environmentally safe criteria for noise in the sea.

9. Milestones:

Phase 1

All scheduled program milestones to date have been met. The acoustic source, incorporating untried technology and design, has been successfully tested at sea. Network design, mechanical endurance testing of receivers, and the data handling/processing architecture have proceeded through all critical review and approval phases on schedule. Ocean climate models have been

developed and in some cases validated with actual data. Finally, permits for network installation and marine mammal research have been submitted. Other major milestones are:

1.	Kauai source & receivers operational	3/94
2.	Pt Sur source & receivers operational	4/94
3.	Phase 1 system fully operational	6/94
4.	Ocean/atmospheric model development	CY94
6.	Altimetry/acoustic data assimilation	CY95
7.	Evaluate Pacific Ocean results	6/95

Milestones: Phase 2

8.	Procure Phase 2 sources/receivers	CY95
9.	Operate SWPAC/Indian Ocean system	CY96-97
10.	Operate Atlantic Ocean network	CY96-97
11.	Operate Arctic Ocean network	CY96-97

10. Transition Plan:

Funded entirely by SERDP, Phase 1 is a basic research experiment in the Pacific Ocean to determine the feasibility of climate trend detection. This phase will underpin the plan needed to proceed, starting in FY95, with Phase 2, the long-term global climate change program, extending to all major ocean basins and assimilating other synoptic data sources. SERDP funding for Phase 2 is included herein. The overall transition plan envisions NOAA assuming funding and management of the long term global monitoring program once all of the elements are in place and functioning.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP (Phase 1)	7000	24000	17000	8000	0	0	56000
SERDP (Phase 2)	0	0	0	10000	10000	0	20000
Total	7000	24000	17000	8000	0	0	76000

12. Performers:

Key scientists from the following research institutions and universities are collaborating in the program: Scripps Institution of Oceanography, Woods Hole Oceanographic Institution, Applied Physics Laboratory/University of Washington, Advanced Research Laboratory/Penn State University, Massachusetts Institute of Technology, Cornell University Laboratory of Ornithology, Hubbs-SeaWorld Research Institute, University of Michigan, Florida State University, Mississippi State University, University of Alaska, Naval Research Laboratory/Stennis Space Center, NOAA Laboratories in Boulder and Miami, Southern Methodist University/Mission Research Corp., Science Applications International Corporation.

Active collaboration is scheduled with Australian, Canadian, French, German, Indian, Japanese, New Zealand, Russian, South African, and Taiwanese scientists. An international Scientific Subcommittee on Ocean Research has been created to plan Phase 2.

13. Principal Investigator:

Dr. Ralph Alewine
Advanced Research Projects Agency (ARPA)
3701 North Fairfax Drive
Arlington, VA 22203-1714
TEL: 703 696-2246
FAX: 703 696-2203

Professor Walter H. Munk
Scripps Institution of Oceanography
9500 Gilman Drive
La Jolla, CA 92093-0210
TEL: (619) 534-5671
FAX: (619) 534-8076

14. Keywords:

Global Warming, Acoustic Thermometry, HIFT, Climate Change, SSAR

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Global Inventory of Biomass Burning

3. **Agency:** Environmental Protection Agency (EPA)

4. **Laboratory:** Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV)

5. **Proposal ID:** #238

6. **Problem Statement:**

Assessment of greenhouse gases, notably, carbon dioxide, methane, nitrous oxide, chlorofluorocarbons and tropospheric ozone, is a primary objective of the U.S. Global Change Research Program (USGCRP) and the Intergovernmental Panel on Climate Change (IPCC). Biomass burning contributes significant amounts of greenhouse gases and reactive trace gases including CO, CO_2, CH_4, O_3,, NO_y, hydrogen, methylchloride and particulates. Up to 40% of greenhouse gas concentrations result from man's fire activities [Andrea, 1991] yet no global program presently exists to monitor this source. The spatial and temporal distribution of biomass burning which is the combustion of vegetation and soils is the key element required to make annual per-country assessments of these emissions. Satellite imagery and remote sensing technology must be used because most of unreported fires occur in remote areas. Gaseous emissions can be computed from physical models of fires, biomass burned and the atmosphere. This proposal details the first plan to build a system to monitor the global distribution in space and time of biomass burning using meteorological satellite imagery, to construct daily maps of fire location and duration for an 18 month period and to estimate the monthly mass of greenhouse gases emitted by these fires.

7. **Project Description:**

Defense Meteorological Satellite Program (DMSP) Data: This Global Inventory of Biomass Burning program will use Operational Linescan System (OLS) data recorded on DMSP satellites. OLS instruments monitor all sources of visible, near-infrared and thermal infrared (TIR) emissions [DMSP Program Office]. The OLS data are unique because the "see" very weak emissions, view them in small pixels across a large scan, and record these emissions onboard the spacecraft during daytime and nighttime. As part of its mission is to record meteorological, oceanographic and solar-geophysical data in support of operational requirements, the DMSP program operates two satellites in sun-synchronous, low altitude polar orbits that carry complementary meteorological instruments, notably microwave imagers and sounders. The National Geophysical Data Center (NGDC) receives, processes and archives all digital data stored onboard all DMSP satellites. This archive program began in 1992.

The Methodology: Fires and other bright lights have been clearly evident in low resolution, visible OLS imagery since the data were declassified in 1977 [Croft, 1978]. We propose to use high resolution (0.5 km) wavelength imagery recorded at night by OLS instruments on two satellites to identify bright pixels on a daily basis. (If high resolution data are not recorded we will use the 2.7 km global data set which includes all fires.) Non-fire pixels will be eliminated

by removing time-stationary sources of light like cities. A daily data base of each fire by location and duration will be constructed for 18 months using existing software to geolocate fire pixels.

The degree of obscuration and scattering of visible, near infrared, and thermal infrared radiation by clouds will be determined from TIR imagery from the same instrument. Fire temperature and subpixel area may be estimated from the OLS imagery, microwave imagery and microwave soundings recorded on the same spacecraft. Daytime images will be searched for the scars or burned area resulting from the fires using either DMSP or LANDSAT data. The amount of biomass burned can then be determined from the area and a model of vegetation. Greenhouse gases emissions will be estimated from two methods. The first will use the number of observed fires, the temperature and duration of each fire, the number of fires estimated to be obscured by cloud cover, and the type of vegetation. The second will use the burn area, the amount and type of vegetation burned and the temperature of the fire. One method will be selected from which monthly estimates of greenhouse gas emissions will be determined for each country for the 18 month period.

Research into the radiative transfer effects of atmospheric conditions on visible, near infrared and thermal infrared radiation observed at satellite altitudes will be conducted at NRL and NGDC. OLS measurements must be corrected for the effects of scattering, diffusion, absorption and reflection by existing clouds and for attenuation by atmospheric water vapor. Complementary instruments exist on all DMSP satellites which provide data to address these concerns for atmospheric modeling and weather forecasting.

A verification program will be established to evaluate the fire locator program and to calibrate the burn area estimates to be derived form the OLS data. This will be performed with a combination of AVHRR and LANDSAT observations and in coordination with current programs in EPA, DOE, DoD and NASA, e.g. EPA is conducting greenhouse gas emission inventories for Russia and sub-equatorial Africa using the OLS Fire product data.

Computer systems required to process the incoming DMSP data as they are received have already been established at NGDC using SERDP funds. Existing software at NGDC accurately references each OLS pixel to a position on the Earth's surface.

Previous Efforts/Accomplishments: It has been demonstrated tat active fires can be successfully detected in nighttime DMSP OLS imagery [Cahoon el al., 1992] and in daytime Advance Very High Resolution Radiometer (AVHRR) imagery from NOAA satellites [Matson et al., 1984]. A method for determining the temperature of subpixel hot spots including fires and subpixel areas of hot spots from AVHRR imagery was defined in Matson and Dozeir, 1981. Fire scars can be seen in imagery from several meteorological satellite programs including OLS [Kroehl, private communication], AVHRR [Flannigan and Vonder Haar, 1986] and LANDSAT [Skole and Tucker, 1993] where burns cover large areas, such as grasslands, savannas, and boreal forests and from OLS and LANDSAT images covering smaller burns such as tropical deforestation. Models to compute the flux of CO, CO_2, CH_4, O_3 and other trace gases and particulate emissions from fires have been developed and tested [Crutzen el al., 1979 and Hao et al., 1991] and from biomass burned [Cahoon el al., 1992 and Justice et al., 1993].

Meteorological satellites offer the advantage of frequent (daily for AVHRR and twice daily for OLS) low cost coverage of active fires on a global basis every day. Because many of the fires in tropical regions are sub-pixel in size, techniques have been developed for converting the fire pixel counts into burn area estimates based on instrument response functions and comparison

with higher spatial resolution data from LANDSAT. OLS imagery are preferred over AVHRR data for this project because the spatial and temporal resolution is much higher, onboard instrumentation provides complementary and essential data, and DMSP imagery are readily and rapidly available from NGDC.

Relationship to DoD/DOE Environmental Objectives: The DOE has a substantial program dedicated to the inventory of data collected by other programs on the amount of greenhouse gas emissions associated with human activities, such as the combustion of fossil fuels. Oak Ridge National Laboratory operates a carbon Dioxide Information Analysis Center (CDIAC) and has been designated as a Distributed Active Archive Center (DAAC) for data on greenhouse gas emissions for the NASA EOS Data and Information System (EOSDIS). The proposed project would contribute a valuable data set on biomass burning for use by DOE scientists.

The U.S. EPA has supported several successful, regional-scale projects to observe biomass burning from meteorological satellite imagery, to conduct field experiments to record the flux of greenhouse gases emitted by different types of fires at different temperatures consuming different fuels and to estimate the annual amount of gaseous and particulate emissions for these regions. NASA GSFC and NASA LRC have cooperated with EPA during similar experiments for different regions to prove that the methodology works.

TASKS:

Task 1- Daily Distribution of Fires: NGDC will develop the procedures for converting OLS data into continuous time series that to be searched for fire signatures. In the DMSP processing scheme, accurate geolocation of each image pixel is fully automated and facilitated by accurate satellite ephemeris and satellite attitude control. A planning workshop will be conducted with participation by all interested parties to define a fire algorithm to be applied to daily imagery.

Task 2- A Fire Detection System and Global Maps: NGDC will coordinate the acquisition of OLS fine data of the world's land surfaces in order to compile a map of time-stationary lights like those from cities and gas flares. A research project directed by EPA will be undertaken to evaluate the possibility of using both the visible and TIR data to enhance the fire detection algorithm. Using data for April and September which are fire active months, we will test the results from Tasks 1 and 2 to locate fires and estimate fire intensity and emissions from existing methods.

Task 3- Development of Cloud Masking Algorithm and Other Meteorological Effects: NRL and NGDC will develop and test an algorithm for the degree and percent of cloud cover in nighttime OLS imagery. NRL will conduct research to investigate the feasibility of retrieving visible and TIR ground-level radiances from nighttime OLS data for use in the fire temperature and fire size algorithms. The results will be compared against the AVHRR method of Matson and Dozier, 1981.

Task 4- Development of Burn Area and Biomass burned Projects: EPA, NRL and NGDC will team in the development of a burn area algorithm and the procedure to compute the burn area on a monthly basis using OLS imagery. A calibration and verification program will be implemented using finer spatial resolution, but coarser temporal resolution,data from LANDSAT and other ground-based and airborne projects already in places to determine the size of fires observed form OLS. This will lead to a set of regionally based calibrations for converting OLS fire pixels into burn area. EPA will lead in the development of land cover map which can be

used to determine the amount of biomass burned. This is an extension of an existing program. From the burn area and the biomass map, NGDC will estimate the amount of biomass burned. Results of Tasks 1-4 will be presented at workshop for peer review.

Task 5- Production of the 18 Month Global Fire Product: After implementing recommendations of the peer review, NOAA NGDC will process 18 months of OLS data to produce the global fire product, i.e., location, intensity and duration of each fire on a daily basis. If recommended by the review, NGDC will also estimate the amount of biomass burned on a monthly basis from the fire product, the burn area and a maps of biomass for the same 18 month period. The 18 month global fire data base will be available on CD-ROM for access by the broader science and IPCC community. NRL and NGDC will develop software to display and analyze a long time series of OLS fire products, plus validation data derived from LANDSAT and other sensors.

Task 6- Greenhouse Gas Emission Modeling: The EPA will use the OLS fire product as a primary input for pyrogenic emission estimated planned for sub-equatorial Africa and the boreal forests of Russia. They will also compute greenhouse emissions from the biomass burned product and compare the results of the two methods for presentation to the peer review committee. Upon successful completion of this modeling, EPA will use a similar method to estimate greenhouse emissions for other countries.

Technical Issues to Overcome: Fires can be readily observed in the nighttime visible OLS data. The major technical obstacle for the project is the accurate geolocation of the OLS data. NGDC is currently conducting research on the geolocation of OLS data, with SERDP support. A state-of-the-art orbital mechanics model has been added to the routine processing and the pixel geolocation program has been updated to more accurately represent the Earth as seen by the OLS. Other potential obstacles, such as developing burn area estimates and modeling greenhouse gas emissions from meteorological satellite observations have been addressed in regional scale projects. Current research projects funded by EPA and ANSA continue to refine and improve the existing models. And finally, the accurate determination of fire temperature and subpixel fire area from the OLS data and complementary data from meteorological instruments onboard DMSP satellites are a part of current research projects.

8. Expected Payoff:

At present there is a dearth of information available on the annual greenhouse gas emissions from fires which remains one of the key uncertainties in our understanding of the global carbon cycle. Basic data on the global spatial and temporal distribution of biomass burning is a prerequisite for the estimation of these emissions. The proposed project will build a global OLS fire product suitable for modeling greenhouse gas emissions through the conduct of an 18 month inventory of biomass burning. It is anticipated that production of the OLS fire product will be continued on an operational basis, with support from civil agencies, such as EPA. The project will contribute to the Committee on Earth and Environmental Sciences (CEES) Global Change Research Program (GCRP) milestones for the development of algorithms for monitoring biomass burning, systems for global monitoring of biomass burning, and the estimation of greenhouse gas emissions from biomass burning. It is anticipated that the global emissions for meeting reporting requirements of the Intergovernmental Panel on Climate Change (IPCC).

9. Milestones:

Three year project milestone chart with the lead center noted.

Quarters: 1 2 3 4 5 6 7 8 9 10 12 13 14 15 16

Task 1 - NGDC X

Task 2 -NGDC X

Task 3 - NRL X

Task 4 - EPA X

Task 5 - NGDC X-----------------X

Task 6 - EPA X------------------X

10. Transition Plan:

The project is designed to meet CESS-GCRP milestone objectives for the development of a global system for monitoring biomass burning. It is anticipated that the funding of an operational OLS global fire monitoring system will be transitioned to the civil agency participants within the GCRP once a successful prototype system is demonstrated.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
NOAA NGDC	446	743	681	335	2205
NRL	49	200	200	151	600
EPA EMSL	105	213	224	86	628
TOTAL	600	1156	1105	572	3433

Each agency is currently engaged in programs that will directly contribute to the Global Inventory of Biomass Burning program, e.g. EPA's modeling of greenhouse gas emissions from biomass burning. They plan to continue those programs at their present level, i.e., $1,000K at EPA, $200K at NGDC and $150K at NRL. We request funding in addition to this level to complete the tasks required to develop, test, and execute a system to monitor greenhouse emissions by country on a global basis each month.

12. Performers:

DoD: Office of Naval Research, Naval Research Laboratory, Washington, DC
NOAA National Geophysical Data Center, Boulder, Colorado
EPA Environmental Monitoring systems Laboratory, Las Vegas, Nevada

13. Principal Investigators:

Dr. Jack Durham
Office of Environmental
Processes and Effects Research
U.S. Environmental Protection Agency
401 M Street, SW.
Washington, DC 20460
TEL: (202) 260-8930
FAX: (202) 260-6370

Dr. James McElroy
EMSL-LV
USEPA
944 Harmon St.
Las Vegas, NV 89119
TEL: (702) 798-2361
FAX: (702) 798-2692

Dr. Phillip Schwartz
Naval Research Laboratory
Code 7213
Overlook Ave, SW
Washington, DC 20375
TEL: (202) 767-3391
FAX: (202) 404-7453

Dr. Herbert Kroehl
NOAA National geophysical Data Center
325 Broadway St.
Boulder, CO 80303
TEL: (303) 497-6121
FAX: (303) 497-6513

14. Keywords:

biomass burning, remote sensing, fire emissions, global emissions inventory, satellite imagery, operational fire product

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Global Environmental Change

2. **Title:** Strategic Environmental Distributed Active Archive Resources (SEDAAR)

3. **Agency:** Navy

4. **Laboratory:** Office of Naval Research

5. **Proposal ID:** #816

6. **Problem Statement:**

DoD resources may be of significant value to the global environmental change research community. Data query and retrieval tools currently exist which promote data archive search. GIS and visualization tools and techniques are available which promote data evaluation and analysis. This SEDAAR activity will promote the use of these tools within the DoD agencies and civilian research communities addressing the objectives of the SERDP activity which includes the acquisition and analysis of data addressing DoD/DOE waste site for the purpose of understanding the impact of initial waste disposal techniques, as well as the effects of waste site remediation efforts.

7. **Project Description:**

This SEDAAR project is an applied research and technology transfer effort whose objective is to implement and demonstrate tools and methodologies which promote the access, acquisition, and use of unclassified and/or recently declassified DoD data and information resources for support of global environmental change research.

The first SEDAAR activity focused on the demonstration Arctic Geographic Information System (GIS) incorporating DoD and civilian data resources. The second SEDAAR activity expanded the scope of the GIS to include coastal regional, site specific, and demographic applications. This specific activity will focus on expansion and population of the GIS in the Arctic and Hawaiian littoral regions in preparation of expansion to other notable sites to be determined with federal agency advisement.

Conceptually, there will be two activity thrusts. These consist of: data/information capture and implementation and demonstration of critical technologies required in the identification, capture, and evaluation of specified data holdings. The SEDAAR effort will provide a database of valuable data and information for the civilian research community and establish "beta" sites using this database in conjunction with a specified analysis tool set. The data and tools will be evaluated to determine their use in addressing the application areas identified.

8. **Expected Payoff:**

This SERDP activity will demonstrate the usefulness of combining recently released DoD data and information with civilian archival data in the analysis of environmental concerns, both local

and regional area coverage. These data will also assist in the understanding of the physical and temporal changes to DoD and DOE waste sites.

Building upon the previously funded efforts, a robust environmental GIS capability will be demonstrated. This can provide users a method to investigate various Arctic and littoral oceanographic and climatic phenomena associated with global climate change. Using existing technology and emphasizing a methodology which captures relevant data, this effort will augment the use of the environmental GIS for investigating: point-source pollution impacts to Arctic and temperate coastal regions; atmospheric phenomena associated with changes in the Arctic environment; and human-induced changes to the Arctic and temperate coastal environment.

9. Milestones:

1.	Kickoff of FY94 SEDAAR3 Project	06/95
2.	Data Access and Interop. Demo	11/95
3.	Database update	01/96
4.	Information Evaluation Demo	03/96
5.	User Workshop	06/96
6.	Database update (2)	08/96
7.	Final SEDAAR Demo	08/96
8.	Final User Workshop	10/96

10. Transition Plan:

The fully developed SEDAAR3 will be tested in the field at locations to be determined based upon the guidance of the DoD. The sites chosen will be a combination of sites from the DoD, other Federal agencies (e.g. EPA, AID, NOAA) and academic institutions. These sites will maintain and update, if desired, the distributed databases and will be independent from the distributed data of the SEDAAR3 effort, which will be maintained at the CIESIN facility in Michigan. This two tier distribution of SEDAAR3 will ensure the continued use by both the DoD and civilian communities after completion of the project.

11. Funding: ($K)

	FY94
SERDP	1250

12. Performers:

This effort will be managed by the the Office of Naval Research (ONR). The Consortium for International Earth Science Information Network (CIESIN), the Naval Oceanographic Office (NAVO), the Defense Mapping Agency (DMA), and the Environmental Protection Agency (EPA) will provide additional technical support.

13. Principal Investigators:

Dr. Scott Sandgathe
Office of Naval Research (ONR)
Code 32
800 North Quincy Street
Arlington, VA 22217-5660
TEL: (703) 696-0802
FAX: (703) 696-3390

Harold Geller
CIESIN
1825 K Street, N.W., Suite 805
Washington, D.C. 20006
TEL: 202 775-6600
FAX: 202 775-6622

Peter Colvin
ERIM
1975 Green Road
Ann Arbor, MI 48105

14. Keywords:

data query, retrieval tools, unclassified data, Arctic Geographic Information System (GIS), databases.

TABLE A-VI FY 1994 POLLUTION PREVENTION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Coatings			
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)	550	632	A-393
Electro Magnetic Powder Spray (AF)	630	124	A-399
Large Area Powder Coating (AF)	315	121	A-403
Alternative Coatings for Cadmium Plating of Small Parts (N)	800	77	A-407
Florinated Ship-Hull Coatings for Non-Polluting Control (N)	895	756	A-412
Organic Protective Coatings and Application Technology (N)	400	65	A-418
Data Base			
Integrated Expert Solvent Substitution Data Base (EPA)	3,000	331	A-422
Diagnostic			
Rapid Testing for Acceptable Materials and Processes (AF)	263	117	A-427
Life Cycle Engineering and Design Program (EPA)	750	304	A-431
Model for Facilities Life Cycle Decisions (EPA)	400	307	A-437
Hazardous Materials Substitutes			
Advanced Zinc Phosphate Metal Pre-Treatment (A)	175	659	A-442
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)	300	673	A-445
High-Performance, Lead-Free Electrical Sealants (DOE)	110	429	A-448
Reduce VOCs and HAPs from Painting and Cleaning Operations (EPA)	600	316	A-451

TABLE A-VI FY 1994 POLLUTION PREVENTION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Hazardous Materials Substitutes			
Aircraft Maintenance Chromium Replacement (N)	180	66	A-455
Dry Nitrogen for Ship Boiler Layup (N)	185	55	A-458
Solvent Substitution and Low VOC Cleaners (N)	150	67	A-460
Hazardous Materials Processing			
Non-Chemical Surface Preparation (AF)	998	130	A-463
Solid State Metal Cleaning (AF)	1,050	116	A-467
Hazardous Waste Reduction			
Large Aircraft Robotic Paint Stripping (LARPS) (AF)	1,940	134	A-471
Laser Cleaning and Coatings Removal (AF)	2,100	139	A-474
Aircraft Depainting Technology (N)	445	81	A-478
Recycle Boiler Nitrite Solution (N)	475	69	A-481
Mixed Waste			
Acid Recycle (DOE)	258	422	A-484
Capacitive Deionization for Elimination of Wastes (DOE)	700	436	A-487
Metal Working Process			
Alternate Electroplating Technology (N)	360	71	A-491
Recycling/Purification of Plating/Cleaning Baths (N)	800	70	A-494

TABLE A-VI FY 1994 POLLUTION PREVENTION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Ordnance Processing			
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)	450	660	A-498
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)	200	680	A-501
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)	350	695	A-503
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N)	3,700	63	A-507
Solventless Pyrotechnic Manufacturing (N)	500	757	A-512
Ozone Depleting Substances			
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A)	400	682	A-517
Chemistry of Halon Substitutes (A)	155	666	A-520
Continuous Aqueous Cleaning to Eliminate ODC (A)	110	634	A-523
Non Ozone Depleting Sealants for Ammunition Applications (A)	250	674	A-525
Replacements of Hydrochlorflurocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)	250	677	A-528
Advanced Streamlining Agent (AF)	850	158	A-531
Encapsulated Micron Aerosol Fire Suppression Technology (AF)	630	113	A-534

TABLE A-VI FY 1994 POLLUTION PREVENTION PROJECTS	Funding $(K) FY94	ID Number	Page Number
Ozone Depleting Substances			
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)	1,000	309	A-537
Pollution Prevention Total	**27,674**		

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** PVD Coatings and ION Beam Processing as Alternatives to Electroplating

3. **Agency:** Army

4. **Laboratory:** Army Research Laboratory - Watertown

5. **Proposal ID:** #632

6. **Problem Statement:**

Goal: Conduct applied research and development to demonstrate that metal or ceramic coatings deposited by physical vapor deposition (PVD), and/or ion-beam-modified surfaces are equivalent or superior in performance and are a cost-effective alternative to electroplated chromium and cadmium for military applications.

Background: Hard chrome is primarily used in DoD related manufacturing to (1) coat high wear surfaces such as bearing shafts and hydraulic components and is principally performed by Original Equipment Manufacturers (OEM's) and (2) rebuild and remanufacture out-of-tolerance components, such as worn shafts and corroded hydraulic components, with the work being performed by maintenance depots. For the former, the use of hard chrome has actually been increasing because the general requirement for coatings has also been increasing due to enhanced performance requirements. For example, one engine manufacturer currently applies hard chrome to 1192 different engine components. For the latter application, many pieces of military hardware are returned to the depots for refurbishment with components that are worn, corroded, or eroded by use. Rather than replacing them, they are reworked by removing the damaged metal, stripping off any old hard chromium coatings, building them up with hard-chrome, and then machining them to final tolerance. As an example of usage, at the Corpus Christi Army Depot, where most of the Army's helicopters are serviced, annually more than 10,000 separate types of components are coated with hard-chrome for this purpose. It should be noted that most of these components are reworked and re-plated several times. To provide an indication of costs associated with chrome plating, it is estimated that for each plating line the cost of waste disposal is $10,000 per month with the total cost associated with installation of a new plating shop that meets EPA and OSHA regulations ranging form $5M to $15M.

Gun tube wear and erosion have been a long-standing military unique problem. A practical objective has been to achieve gun tube wear life comparable to fatigue life. The unexpectedly short tube life for the new 8" and 155 mm gun systems was revealed by wear and erosion test late in the development cycle. Further, the Army has a strong interest in pushing towards higher gun performance to extend the range of its artillery and to obtain higher velocities and shorter times of flight for rapid-fire anti-aircraft guns. The problem remains to obtain acceptable tube life with higher performance. Modern high performance guns require erosion protection, and advanced gun systems under development (such as Liquid Propellent and Rail Guns) will push these requirements to even higher standards. Chromium plating of gun tubes has provided a finite improvement in tube life depending on gun operating conditions. But the mechanical stability of Cr electroplate (due to numerous microcracks) is limited and new protective coatings with even higher melting points (refractory metals) are needed to challenge

the use of more energetic propellants which have higher flame temperatures. Reduction in the use of electroplated chromium will result in an appreciable reduction of the Army's cost of safe handling and disposal of hazardous waste (estimated to be greater than $335M in 1991).

Cadmium electroplating is also used by both OEM's and by DoD maintenance depots to impart corrosion resistance and lubricity to a wide variety of parts, although substitute coating processes have been more fully developed for this than for the hard-chrome plating. These alternatives include electrodeposited Zn alloys and ion-vapor-deposited (IVD) aluminum. The Air Force has taken the lead in the actual implementation of these alternatives. At other facilities, such as the Cherry Point Naval Aviation Depot, which has had an IVD system for almost 10 years, the ratio of Cd-plated to IVD-coated parts is more than 10 to 1. The Anniston Army Depot, Anniston, Alabama, has recently installed two IVD systems and is replacing cadmium with IVD aluminum for certain components of armored vehicles other than fasteners. The Air Force acknowledges that IVD-Al will not replace more than about 50% of the Cd-plating requirements. The Army has authorized electroplated zinc as an alternative to cadmium for grade 8 fastener application. Concurrence by the Air Force and Navy to accept zinc as a legitimate alternative to cadmium for these fasteners has also been obtained. Exceptions include selected electrical or electronic applications where cadmium-plated fasteners are required or preferred and high-strength steels for certain helicopter components. A recent preliminary laboratory study by the Army Research Laboratory, Watertown Site, showed a Zn-Ni alloy provided better resistance than zinc and exhibited a comparable coefficient of friction. Thus there still exists the strong need for further coating development efforts.

7. Project Description:

Previous Efforts: Most previous efforts in this area have been the investigation of alternative electroplated coatings, such as Zn alloys to replace cadmium. The only significant exception to this is the development of IVD aluminum. It is interesting to note that large-scale IVD-Al systems have been available for over 15 years, yet DoD is still funding R&D work to investigate and implement this process. Electroless nickel coatings are also being investigated as a replacement for chrome, but nickel is on the EPA "toxic enemies" list so it should only be considered as an interim replacement process.

Technical Objective: Demonstrate PVD coating techniques and ion beam processing as effective environmentally acceptable alternatives to chromium and cadmium electroplating. Demonstrate applicability to advanced military systems, and the ability to withstand severe military service conditions.

Technical Approach: Vacuum-based PVD coating techniques are known to produce the highest quality coatings, with widespread use of high vacuum techniques in the microelectronics industry having broadened the industrial base for large scale systems with a concomitant reduction in cost. The most advanced types of PVD coating techniques utilize what can be called "ion-assist" whereby energetic charged particles are incident on the workpiece during the coating process. Two variations on ion-assisted PVD are (l) ion-beam-assisted deposition (IBAD) whereby a directed beam of energetic particles from an ion gun are coincident on the workpiece with the depositing vapor atoms, and (2) magnetron sputtering whereby vapor atoms are produced by sputtering from an electrode with ions being accelerated from a plasma by application of a negative bias to the workpiece. These two techniques produce coatings that are highly adherent, fine grained, generally pin-hole free and fully dense, and which can be deposited at relatively low temperatures on virtually any type of solid material. The deposition

rates for these types of coating techniques are sufficiently high that they could be expected to economically replace both chrome platings deposited by OEM's and electroplated cadmium. for these applications, the types of coatings to be investigated would be TiN, (Ti, Al)N, CrN, Ta and diamondlike carbon, all of which have been previously investigated for corrosion and wear applications. However, the deposition rates are not high enough to replace the chrome plating operations in military depots which are intended for re-build of components. For this application, the proposed solution is to rebuild the component using an alternative electroplating technique such as electroless nickel, machine it to final tolerance, and then apply one of the above PVD coatings which should provide significant wear and corrosion resistance leading to a reduced requirement for future rework.

Ion implantation has been shown to significantly improve the corrosion and wear behavior of a variety of materials. With this technique near-surface alloys or compounds can be produced, with no discrete interface between the modified layer and underlying material that could lead to delamination problems as is possible with coatings. Virtually any element can be implanted into substrate materials although only a few will be selected for this program. Previous research conducted at ARL has shown that nitrogen implantation into hard-chrome coatings increases the surface hardness and significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses. This will be further investigated under this program as well as ion implantation of thin-dense-chrome coatings, a proprietary process of Armoloy, Inc., which is an electroplating process that does not produce toxic effluents.

Relationship to DoD Environmental Objectives: This program addresses the objectives of eliminating airborne toxic emissions and hazardous waste streams associated with chromium and cadmium electroplating. The treatment of these hazardous effluents at the many installations utilizing these processes is estimated to cost DoD tens of millions of dollars each year.

Relationship to Other Similar Ongoing Work: In November 1992 the Basic Industry Research Laboratory (BIRL) at Northwestern University was notified by ARPA that they will be awarded a substantial contract ($1.5M over two years) entitled, " Hard-Chrome Coatings: Advanced Technology for Waste Elimination." A major portion of this contract will be to investigate methods for reclaiming or recycling effluents from the plating operations. Another significant portion is the investigation of alternative coating processes. These include HVOF plasma spraying, laser cladding, laser-assisted chemical vapor deposition, and sputtering. The Surface Modification Branch at NRL will have a small effort under the DARPA program ($30K per year) to perform ion-beam modification of some of the coatings. This proposed SERDP program is designed to investigate other coating techniques and thus there would be virtually no duplication of effort. One of the POC's (BDS) on this proposal has previously collaborated with the PI on the ARPA contract in other areas and it is anticipated that there would be extensive collaboration between the two programs to ensure that DoD would obtain the optimum solution(s) to this problem.

Tasks/Activities: Since it will not be necessary to demonstrate that the coating techniques to be investigated under this program are environmentally acceptable, the focus of the project will be the characterization an evaluation of the coatings in comparison to electroplated chromium and cadmium coatings. Evaluation of coating performance must include laboratory simulation of the conditions to which coated components will be subjected to in battlefield and global environments, with a baseline comparison with hard-chrome coated components. Properties such as hardness, adhesion, and density will be determined for all of the coatings. Measurements

related to actual performance will be correlated with the type of electroplated coating intended to be replaced and the actual enduse application. Thus, appropriate tests could include (l) sliding wear tests with realistic loads, speeds, and use of lubricants, (2) erosion tests, (3) corrosion tests using electrochemical and/or salt spray methods, and (4) low-cycle or high-cycle fatigue, or rolling-contact fatigue, and (5) Hothardness tests.

In addition to evaluation of coated test coupons, actual components will be selected for coating and evaluation in rig tests at appropriate depots. The POCs have assembled a team that can address all of the tasks related to coating deposition, characterization, and evaluation. The following correlates the tasks with the activities expected to perform them. An (A) or (N) following the activity denotes whether the Army or the Navy will be the primary contact with the activity.

1. Corrosion Science Group, ARL(A): Deposition of IBAD and plasma sprayed coatings; cohesion, adhesion, and porosity measurements on all coatings; surface analytical measurements; corrosion by electrochemical impedance spectroscopy, galvanic corrosion studies; erosion tests; coefficient of friction measurements; rolling contact fatigue measurements.
2. Surface modification branch, NRL(N): Deposition of IBAD coatings; hardness, density, and adhesion measurements on all coatings; composition measurements on compound coatings and determination of impurities, if any; other surface analytical measurements; sliding wear tests; electrochemical corrosion tests.
3. BIRL, Northwestern University: Deposition of magnetron sputtered coatings; high temperature wear tests using Falex tester; deposition of HVOF coatings (A).
4. Jet Process Corporation, New Haven, CT: Deposition of PVD coatings (N).
5. Armoloy of Connecticut, Inc.: Deposition of TDC coatings (A)
6. Naval Air Warfare Center, Trenton, NJ: Fatigue testing of coated samples (N).
7. Corpus Christi Army Depot (CCAD): Deposition of cadmium and chromium coatings onto test specimens selection of two helicopter engine or transmission components (in consultation with ARL) for coating; rig testing of coated components (A).

In addition, in the latter stages of the project, attempts would be made to perform actual flight tests on coated and surface modified components. The arrangements for these would have to be made in cooperation with the Army Aviation Systems Command and the Naval Air Systems Command.

Technical Issues to Overcome: An important issue in developing new types of coatings in any system is whether it will have any effect on any other system components. As an example, a part that is currently chromium-plated may be in sliding contact with another part in an aircraft engine. If the chromium coating is replaced with another coating which demonstrates superior performance in laboratory tests, will it have a detrimental effect on its mating part? This potential problem will be considered in the selection and evaluation of actual components. This overall program is considered to be of medium technical risk.

8. Expected Payoff:

Impact: The costs of alternative coating technologies should not be compared with the previous cost of chrome and cadmium coating, but with the expected future costs associated with the processes, taking into account regulations projected into the future. The Basic Industry Research Lab has performed a detailed cost analysis based on information provided by CCAD and McClellan AFB and on their own calculations related to PVD coating operations and have

concluded that for operations that would produce equivalent throughput, the total annual operating cost for a PVD facility would be approximately 20% less than for a plating operation.

Coatings developed under this project should demonstrate performance that exceeds that of electroplated coatings, thus reducing the frequency of rework necessary. This will further reduce the costs associated with the new processes. As an example, if a 2.5 X increase in service life by using ion implantation can be achieved, estimates based on CCAD data show these re-work savings on only three bearings and gears used in the AH-1/UH-1 helicopter drive trains would total over $1.2 M yearly. The potential on a DoD wide basis would be many times greater.

9. Milestones:

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                                          Year 1        Year 2        Year 3
                                         2Q 3Q 4Q 1Q 2Q 3Q 4Q 1Q 2Q 3Q 4Q

Test coupon fabrication                  S---C
Coating applic. to coupons           S---C
Lab. wear evaluation                 S------------C
Lab. electrochem. eval.                    S------------C
Fatigue evaluation                       S-----------C
Salt-Spray evaluation                          S-----------C
Component selection            S---C
Coating optimization ident.                     S--------C
Coating components                                     S----------C
Rig testing                                                   S-------------C
Develop transition plan                                       S--------C
Flight testing                                                S--------C
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S=START C=COMPLETE

10. Transition Plan:

There are an extremely large number of potential users of the technology developed under this program. Virtually all military that overhaul aircraft, land vehicles, or ships perform chromium and/or cadmium electroplating. In addition, many OEM's can benefit from this technology since chromium and cadmium are still being applied to components during the manufacturing process. It is also intended to spin-off this technology into areas related to armaments, e.g., gun tubes which are routinely electroplated with chromium to provide wear resistance to portions of the bore.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
Corrosion Science Group Surface Science, ARL	240	270	240	750
Surface Modification Branch (NRL)	245	280	245	770
SERDP Total	485	550	485	1520

In addition, from the above amounts, funds would be provided to the other organizations listed above in the Tasks/Activities Section on a service basis. In general, the amounts would range from $10K to $30K per year for each organization. It is anticipated that approximately 67% of the total funding would remain in-house at ARL and NRL, with the remaining 33~ distributed to the other organizations.

The FY94 funding would be entirely from SERDP, although other agency funds would be solicited as a supplement.

Based on the results of the work performed under this project, a detailed transition plan would be developed early in 1995. This would be done in close cooperation with the field activities, CCAD and CPNAD, that took part in the program. In addition, there would be the coordination with other activities such as Army MSC's and RDEC's, NAWC's as well as the Joint Technology Exchange Group and the Aerospace Chrome Elimination Group (government and industry). Additional components beyond those evaluated in the project would be selected and then pilot production quantities of all components would be coated, with some subjected to additional rig testing (e.g., engine evaluations on a test stand) and the remainder installed in actual operating aircraft. Cherry Point NAD expects to install a large PVD coating system in early 1995, which should coincide well with the transitioning of the technology. Since it will not be possible to individually evaluate (qualify) the replacement coatings for every component that is currently electroplated, a key aspect of the transition plan would be to provide information and data, including coating deposition specifications, to agency engineers so that new coating technologies can be certified for use in broad areas.

12. Performers:

See the Tasks/Activities section above. Since there is intended to be mutual sharing of information between this project and the ARPA project, and since many OEM's are facing the same hazardous effluent emission restrictions as military installations, it is believed that by the time of completion of this program, there should be a strong possibility for implementation of Cooperative Research and Development Agreements (CRADA's) with some of the OEM's.

13. Principal Investigators:

John H. Beatty
AMSRL-MA-MA
Army Research Laboratory
Watertown, MA 02172-0001
TEL: (617) 923-5212/5331
FAX: (617) 923-5219
E-mail: jbeatty@watertown-emhl.army.mil

Bruce D. Sartwell
Surface Modifications Branch
Naval Research Laboratory
Code 6675
Washington, D.C. 20375-5345
TEL: (202) 767-4800
FAX: (202) 767-5301

14. Keywords:

Hard chrome, physical vapor deposition, metal coatings, ceramic coatings, electroplated chromium, ion-beam-modified surfaces, zinc alloys, tin alloys

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Electro Magnetic Powder Spray

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory

5. **Proposal ID:** #124

6. **Problem Statement:**

The goal of this program is to development environmentally benign materials and processes to deposit or remove chromium, nickel, or copper on metal parts.

New technology is needed as an alternative to traditional electroplating and plating removal methods which depend heavily on use of hazardous and toxic materials and generate volumes of hazardous wastes which must be managed, treated and disposed of. A number of alternative technologies are being pursued within the government and the private sector which eliminate the need for toxics use and generation. Many of these involve flame or plasma deposition. Wright Laboratory has participated in many of these development efforts. Review of research sponsored or performed by the Department of Energy and other researchers has generated interest by Wright Laboratory in a potential "leapfrog" technology based on very high energy deposition using a rail gun concept. The potential exists for using pulsed power sources for high density powder consolidation and deposition on a variety of substrates. Railgun technologies have a major advantage over other accelerator technologies in that the acceleration of the models can be kept under complete control throughout the acceleration process. Experimental results to date suggest that high-energy high-rate processing in this manner promises a novel, environmentally benign means of metal surface modification.

This is a FY93 funded SERDP Project requiring FY94 continuation.

7. **Project Description:**

Technical Objective: The objective of the planned effort is to develop and introduce new technology to deposit and strip coatings of copper, nickel, and chromium from metal parts, especially aircraft engine parts, such as shafts, gears and vanes.

Technical Approach: The proposed project will involve research and development in use of hypersonic energy techniques to (1) deposit material on selected aerospace parts and (2) remove material deposited by such techniques. Study will be conducted of the physical and chemical basis for this potential breakthrough technology. Considerations in identifying an acceptable technology will include: maintenance or improvement of product quality and performance in connection with both deposition and removal; effects of part geometries on process effectiveness (especially thickness); process reliability and quality assurance, and environmental health and safety. Research findings associated with the rail gun concept will be assembled and evaluated. Development needs will be

product quality and performance in connection with both deposition and removal; effects of part geometries on process effectiveness (especially thickness); process reliability and quality assurance, and environmental health and safety. Research findings associated with the rail gun concept will be assembled and evaluated. Development needs will be identified and implemented. An optimum technical approach will be developed, scaled up, demonstrated and qualified. As previously stated, needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

Research on the subject of rail gun technologies has been performed by AF Aero-Propulsion Laboratory, US Department of Energy, University of Texas, Aberdeen Proving Grounds and others. No other government or industry sponsored work is known to be ongoing or planned dealing with hypervelocity deposition of copper, nickel, and chromium for industrial applications.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment associated with traditional electroplating processes.

Planned efforts on solid state cleaning will feed into the overall processes to be developed by this effort. Wright Laboratory EOARD work with Technion in Israel and investigation of thin film deposition technologies are also relevant. AF Civil Engineering Support Activity (AFCESA) spray casting development efforts also bear on the proposed effort.

Tasks/activities: Process studies will be conducted to identify and assess candidate technologies for both deposition and removal. Studies of development needs will be identified and implemented. The most promising technology alternatives will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed which will include production cost estimates. Prototype will be transitioned to users for extended production evaluation. Needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

Technical issues to overcome: New technology must be developed that is environmentally acceptable and affordable and able to compete with technologies that have been used and optimized over more than 40 years. The concept is innovative and the risks are high, but the potential payoff justifies the investment. The principal technical issue is to develop optimum parameters for material condition, impact velocity, current waveshape, target condition and distance, target temperature, and chamber atmospheric conditions.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.A.3
Requirements Category:	I.3.f-i
Work effort:	Tech Base

8. Expected Payoff:

Availability of usable non-electroplate deposition\removal processes to the aerospace industry will free Air Force and industry users from the burdens of using a technology dependent on chromates and cyanides. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

The planned effort will be redirected or terminated if it involves unavoidable adverse impact to weapon system efficiency, capability, or schedule. If successful, the effort will provide a cost effective and environmentally safe alternative to use of toxic materials and processes.

9. Milestones:

1.	Initiate project. Initiate studies to define deposition process physical and mechanical characteristics, to define critical process parameters for both deposition and removal, and determine materials properties	07/93
2.	Complete definition studies. Initiate selection of parts and processes to be targeted for development and application of the new technology. Initiate preparation of experimental design for initial technology demonstration.	09/93
3.	Finalize deposition technology demonstration agenda. Select site for deposition demonstration. Initiate preparations for technology demonstration	11/93
4.	Conduct deposition technology demonstration. Initiate analysis of results in concert with research partners and user technical representatives.	03/94
5.	Initiate studies of removal process options. Design and initiate tests and experiments to address removal effectiveness and effects on integrity of coated parts.	09/94
6.	Initiate validation studies for both deposition and removal processes to address materials performance and integrity, process quality and consistency, and system performance validation.	11/94
7.	Complete validation studies. Determine if scale up studies are warranted. If so, develop and initiate a pilot scale demonstration plan aimed at determining full scale process requirements and characteristics.	03/95
8.	Complete pilot scale demonstration plan. Initiate actions to perform pilot scale demonstration.	04/95
9.	Complete pilot scale demonstration. Review results with users and research partners and determine whether full scale demonstration is warranted.	09/95

10. Transition Plan:

Following decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (Air Logistics Center or DMMF at Wright Patterson AFB OH). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will then be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

Potential users will be an integral part of the R&D effort for its duration. Their participation and technical inputs will be utilized throughout the technology development and validation process.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	300	630	630	1560

12. Performers:

The project will be performed under the technical leadership and direction of:
Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate, Wright-Patterson AFB, OH 45433. The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB Ohio.

13. Principal Investigator:

T. J. Reinhart
WL/MLSE
Wright-Patterson AFB, OH 45433-6703
TEL: (513) 255-3691
FAX: (513) 476-4419

14. Keywords:

Chromium, Nickel, Electroplating, Plating removal, Rail gun, Pulsed power sources

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Pollution Prevention

2. Title: Large Area Powder Coating

3. Agency: Air Force

4. Laboratory: Wright Laboratory, Aeronautical Systems Center

5. Proposal ID: #121

6. Problem Statement:

Current surface coating technologies for aerospace systems employ spray application processes which use and release volatile organic compounds (VOCs) or isocyanates.

Existing primers and topcoats are solvent based systems which have offered excellent protection against corrosion or other operating environment conditions. However, industrial use of solvent based technology has numerous drawbacks: evaporation of toxic volatile organic compounds (VOCs), release of toxic isocyanates, low transfer efficiency, and relatively long cure times. An alternative technology, use of powder coatings, has generated considerable interest within the aerospace industrial community. Powder coating typically involves electrostatic application of powdered metal to a grounded part, followed by a curing cycle to flow the material into a continuous coating. Advantages of powder metal technology include: reduction of toxics use and generation, increased transfer efficiency, and reduced costs of environmental safety and compliance and energy use. Current technology has limitations, however, in use of powder for large parts, such as those on the outer moldline of aircraft. Technology development is needed to obtain the full benefit of powder coatings use in this area of aerospace manufacturing.

New project or enhancement: This proposal requests FY94 funding to continue a FY93 funded SERDP.

7. Project Description:

Technical Objective: Technology for large area powder coating will be developed, optimized, reduced to practice, and qualified for use on Air Force systems.

Technical Approach: This program is an integrated program to develop alternatives to solvent based coating systems for large aircraft parts. Considerations in identifying an acceptable technology will include: maintenance or improvement of substrate integrity, effects of part geometries, process quality assurance, and curing specifications. Candidate technologies, including both government and industry initiatives, will be identified and assessed. Development needs will be identified and implemented. Most promising technologies will be developed, optimized, scaled-up, demonstrated and qualified. Needs

of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

The planned effort will be coordinated with Wright Laboratory continuing work on advanced low VOC and powder coating programs.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment.

The proposed effort is relevant to various Air Force and industry efforts to develop powder metal technologies for aerospace use. The needs of ALCs are sufficiently urgent to warrant Wright Laboratory participation in the quest for acceptable large area powder coating technology.

Tasks/activities: Process studies will be conducted to identify and assess candidate technologies, including both government and industry initiatives. Studies of development needs will be identified and implemented. The most promising candidate technology will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed. Prototype will be transitioned to users for extended production evaluation. Needs ALCs and GOCOs will be given priority attention.

Technical issues to overcome: Major technical issues include: powder formulation, powder handling and storage, meeting low temperature flexibility and reverse impact requirements, maintenance of proper coating quality and thickness, and curing optimization.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.B.1
Requirements Category:	3.I.4.a
Work effort:	Tech Base

8. Expected Payoff:

Availability of acceptable large area powder coating technology will liberate Air Force and industry users from the burdens of using a technology dependent on VOCs and air toxics. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

The planned effort will not adversely impact system efficiency, capability, or schedule. Experience with detail part technologies suggests that costs may be lower.

9. Milestones:

1.	Initiate project Initiate studies to define powder coating process mechanisms and requirements for large area coating. Select demonstration site and mobilize R&D team. Design and initiate tests and experiments to determine materials properties	10/93
2.	Complete definition studies. Initiate selection of parts and processes to be targeted for development and application of the new technology. Initiate preparation of experimental design for initial technology demonstration	04/94
3.	Finalize deposition technology demonstration agenda. Select site for deposition demonstration. Initiate preparations for technology demonstration	06/94
4.	Conduct deposition technology demonstration. Initiate analysis of results in concert with research partners and user technical representatives	12/94
5.	Complete review of technology demonstration results. Initiate validation and optimization studies Initiate experiments to determine effects of processes on substrates/parts Evaluate process quality and consistency	02/95
6.	Complete validation and optimization studies Initiate planning for scale-up studies determine full scale process requirements in terms of equipment, personnel, siting, and operating processes	12/95
7.	Complete scale-up planning Initiate acquisition and positioning of scale-up elements	02/96
8.	Conduct pilot scale demonstration Review results and determine if full scale is appropriate	11/96

10. Transition Plan:

Following decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (ALC or GOCO). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

Degree of coordination conducted between performer and user: Potential users will be an integral part of the R&D effort for its duration. Their participation an technical inputs will be utilized throughout the technology development and validation process.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	100	315	480	895

12. Performers:

The project will be performed under the technical leadership and direction of:

Air Force Material Command
Aeronautical Systems Center
Wright Laboratory
Materials Directorate
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration tasks.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the pilot and full demonstration site to be either an Air Force Material Command Air Logistics Center, the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio, or a selected Air Force GOCO facility.

13. Principal Investigator:

T. J. Reinhart
WL/MLSE
Wright-Patterson AFB, OH 45433-6703
TEL: (513) 255-3691
FAX: (513) 476-4419

Wright Laboratory has extensive research and development experience in the area of application and fusing of powdered thermoplastic materials on metallic/non-metallic substrates. Wright Laboratory also has extensive long term research and development experience with powder and other coatings technology. Many of the DoD specifications involving coatings technologies have been developed by and are under the jurisdiction of Wright Laboratory.

14. Keywords:

Coating, Powder metallurgy, VOCs, Isocyanates, air pollutants, painting

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Alternative Coatings for Cadmium Plating of Small Parts

3. **Agency:** Navy

4. **Laboratory:** Naval Sea Systems Command

5. **Proposal ID:** #077

6. **Problem Statement:**

Cadmium is an environmentally unacceptable material that also poses a threat to worker health. Cadmium is considered such a threat to workers that the Occupational Safety and Health Administration (OSHA) recently revised their cadmium regulations. OSHA, in its September 14, 1992 "Occupational Exposure to Cadmium; Final Rules," reduced the allowable airborne concentration of cadmium in the workplace by 95% (from the previously accepted Permissible Exposure Limit or PEL). Compliance with the OSHA Cadmium Standard is expected to cost domestic industries $159 million/year. The United States Navy, as a cadmium user, will be forced to pay more to purchase, handle, and dispose of this toxic heavy metal.

The environmental unacceptability of cadmium has prompted many other countries to develop regulations or "bans" on the material. For example Sweden enacted a comprehensive cadmium ban in 1985. Finland also restricted cadmium usage in 1992 and Germany has prohibitions against the use of some cadmium compounds.

The United States Navy has already identified cadmium as a problem and tried to eliminate requirements for this toxic heavy metal. The principal example of this effort is the reduced use of cadmium plated fasteners.

Unfortunately, some cadmium-alternatives are still hazardous materials. For many common small parts, the cost-effective alternative is a zinc or zinc alloy system (e.g., tin-zinc, zinc-cobalt). While these systems may be cost-effective substitutes, zinc is beginning to appear in regulatory statutes as a controlled substance (e.g., California Title 22, Land Disposal Regulations). As such, using cadmium alternatives based on "listed" hazardous materials represents only an interim step. To remain cost effective, the Navy must identify high performance cadmium substitutes that are unlikely to be affected by current or future environmental laws.

7. **Project Description:**

The project intends to focus on the development of environmentally acceptable alternatives to cadmium coatings through the proposed research category of 6.2/6.3. This

project addresses the requirements of subthrust 3.A.3: Plating and Finishing (3.I.3.g). Cadmium coatings provide a designer a surface coating/ surface treatment to control corrosion and provide other engineering properties to components manufactured from various materials, most often carbon steel. Without a cadmium coating, a designer may consider an alternative base material, thereby increasing the cost of the component. Alternative base materials to carbon steels include 300 series stainless steel alloys, nickel-based alloys, or titanium alloys.

The availability of environmentally benign methods to provide corrosion control or other functional engineering properties to metallic components can be critical. Consider a system using a significant, cadmium plated, carbon steel component with critical strength and fracture toughness properties. The cost of system modification to use a different material can be significant, including costs for research and development, testing, raw materials, and production. Ideally there would be an alternative to the common types of protective coatings/treatments used before the arrival of the current hazardous material regulations. The critical properties to be duplicated would be corrosion control, the ability to be applied at thin films, compatibility with paint systems, and lubricity.

Some non-carbon steel components also receive a surface coating or treatment based on hazardous materials to afford various engineering properties. Examples include cadmium on aluminum or stainless steel connector back-shells for lubricity or anodizing processes for corrosion control or galvanic compatibility of aluminum and titanium.

Problems may also arise where a developer uses an alternative base material, such as titanium, for carbon steel (e.g., on fasteners). This can lead to a galvanic compatibility problem with surrounding materials. The problem may be mitigated by surface anodizing and coating with a dry film lubricant. However, the dry film lubricant typically used can be high in volatile organic compounds, hazardous air pollutants, and heavy metals. Thus the attempt to mitigate one environmental problem can result in another.

The specific program objectives include: 1) identify promising corrosion control coatings or substrate treatments that are not based on hazardous materials (i.e., cadmium, chromium, nickel, lead, or zinc); 2) develop the processes required to create coating systems that duplicate the corrosion control and critical engineering properties of cadmium (e.g., lubricity); 3) evaluate the performance of these alternatives under simulated Navy operational conditions for corrosion control, lubricity, wear resistance, adhesion, coating compatibility, and influence on substrate material properties (i.e., fracture mechanics); and 4) collect cost data that will allow economic assessments of alternative coating system performance.

It is proposed that the project will focus on duplex systems formed from chemically or physically deposited (CVD, PVD) materials that, by design, will meet or exceed the typical properties afforded to metallic substrates by typical cadmium coatings (QQ-P-416). CVD/PVD coatings offer a designer benefits by being applicable to surfaces of complex shape and being environmentally benign processes.

To-date the idea of duplex CVD/PVD system for corrosion control applications has not been fully explored. A primary use of CVD coatings has been for enhanced wear resistance of carbon steels in non-corrosive applications.

An example of a duplex system of interest is that consisting of a base coat of titanium nitride (TiN) and a topcoat of PVD aluminum or aluminum alloy. TiN coatings have been used extensively in the machine tool industry as a thin film, wear-resistant coating. The coating is deposited by a chemical vapor deposition process (CVD). The basic coating is inert in the marine environment and would protect a steel substrate to the extent that it forms a barrier to the atmosphere. In most applications, the coating is porous. To protect against corrosion at the pores in the thin film, the TiN would be topcoated with PVD aluminum or aluminum alloy. The PVD aluminum would be expected to provide the sacrificial protection necessary for corrosion control at the pores. Given the excellent adhesion and wear resistance of the TiN, the duplex system would be expected to be tenacious. Excessive wear may remove the uppermost layers of aluminum, yet would not be expected to remove the aluminum from the critical areas of the TiN pores.

The project would include the development of a comprehensive matrix of alternative surface coatings/treatments. The matrix would include TiN, silicon nitride, PVD aluminum, and PVD aluminum alloys. The matrix would include Military standard cadmium and zinc platings as controls and alternative base materials, such as carbon steel, 316 stainless steel, high nickel alloys, and titanium materials. Materials included in the test matrix will be evaluated concerning performance and cost. Rough cost data will be collected for all coating systems during test matrix development. The cost data will be presented as "cost factors" relative to the current overall life-cycle expenses associated with cadmium (i.e., cradle-to-grave).

A CVD/PVD coating process specification will be developed and trials conducted to determine the critical process control parameters to achieve a high quality coating. During this phase of the testing, the surface coatings/surface treatment systems will be applied to carbon steel test coupons and the operational parameters varied (e.g., chamber vacuum, surface cleanliness, ionization parameters). The samples will be subject to QA tests including electrochemical tests to quantify the material corrosion resistance, wear and lubricity tests, and metallurgical inspections (i.e., Auger, SEM). The QA tests will characterize the best performing coating systems and the key process control parameters. The QA tests are not intended to fully qualify a process, but to narrow the test matrix for more extensive testing of several samples.

Provided with this data, several samples of more complex forms will be coated and subject to a battery of simulation tests. In this phase the surface coatings/surface treatments will be applied to carbon steel, stainless steel, nickel-base and titanium alloys. The simulation tests will include marine atmosphere exposure testing (with and without organic coatings), immersion tests, torque-tension testing (as fastener coatings), destructive metallurgical examinations to determine coating uniformity across complex surfaces (including blind holes), and rising step load tests. The exposure and immersion tests will document the general corrosion resistance afforded by the coatings/treatments both to the base material and also any galvanic interaction to a dissimilar metal coupled to the

coated/treated material. The torque-tension tests will investigate lubricity properties of the coatings/treatments. The destructive inspections will provide data on the limitations of the process to coat/treat complex geometries. The rising step load tests are design to provide K_{ISCC} data to determine if the coatings/treatments can cause environmentally assisted cracking of high strength materials.

A natural marine atmosphere exposure shall be used to evaluate corrosion control performance. In addition seawater shall be used in all cracking and embrittlement studies. Sufficient replicates shall be used to develop statistically significant data. The exact number of replicates and statistical approach used shall be developed as the program evolves.

8. Expected Payoff:

The result of the program shall be the development of a new, thin film, surface coating/treatment that provides corrosion control and selected engineering properties (e.g., lubricity) for high value, small parts. The coating will allow for the reduction in use of hazardous materials like cadmium and zinc.

9. Milestones:

1.	Start selection of duplex system.	10/94
2.	Complete selection of duplex systems.	11/94
3.	Initiate process characterization.	11/94
4.	Start process QA tests.	2/95
5.	Finalize optimal system selections.	4/95
6.	Prepare complex test samples.	4/95
7.	Initiate detailed testing.	6/95
8.	Complete electrochemical tests.	8/95
9.	Complete torque/tension tests.	8/95
10.	Provide interim report.	9/95
11.	Complete rising step load tests.	12/95
12.	Complete field immersion exposures.	6/96
13.	Final report.	8/96

10. Transition Plan:

The transition plan will be facilitated by the process development procedures that will include the use of commercial industries to prepare test samples by Navy specifications. This insures the eventual production capability. Funding-in-kind will be expected from the contributing coating preparation groups. Developing the process in this fashion will simplify the transition to a Navy-wide process. The Navy will select high-value, small parts as candidates for the coating through consultation with the NAVSEA HM&E and weapon systems design engineers. The parts will be coated by the best practices developed and subjected to fleet trials. These trials will qualify the utility of the process for widespread Navy, DoD, and industrial use.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	800	0	0	0	800
Navy	100	300	200	50	650
Total	900	300	200	50	1450

12. Performers:

The principal Navy performers will the Naval Sea Systems Command and the Naval Research Laboratory. Private industry will be represented by the Ocean City Research Corporation and Titanium Finishing Corporation.

13. Principal Investigator:

Mr. A. Richard Parks
Department of the Navy
Naval Sea Systems Command, SEA 03M1
2531 Jefferson Davis Hwy
Arlington, VA 22242-5160
TEL: (703) 602-0214
FAX: (703) 602-0247

14. Keywords:

Cadmium, Plating, Environmental, Corrosion, Wear, Lubricity.

SERDP FY94 Proposal

1. SERDP Thrust Area: Pollution Prevention

2. Title: Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control

3. Agency: Navy

4. Laboratory: Naval Command, Control and Ocean Surveillance Center, and Naval Research Laboratory

5. Proposal ID: #756

6. Problem Statement:

The goal of this project is to develop non-polluting fouling resistant or fouling release hull coatings exploiting the low surface energy of surface oriented perfluorinated alkyl compounds. This project is a continuation of the FY93 funded "innovative Very Low VOC Antifouling Paints and Processes" SERDP (6.2) program, and includes a new initiative in cooperation with NRL to explore the fouling release properties of low-glass-transition-temperature polyurethanes that have liquid-like surfaces. This project meets SERDP Pollution Prevention Objective 3 and associated with RELIANCE thrust area 3.b (Coatings and Treatment). It addresses the specific Navy requirements 3.I.8.h (Prevention of hazardous discharge from ship in-water hull cleaning).

Protection of ship-hulls from marine fouling organisms is essential for efficient fleet operation and energy conservation. To achieve this protection, ship hulls have been coated with antifouling paints that contain toxic material such as cooper or organotin. Conventional antifouling coatings create an environmental hazard due to continuous release of toxic materials. A cruiser size ship (35,000 ft^2 hull area) releases approximately 2 lb cooper/day that may bring approximately 5 million gallons of sea water to toxic copper concentrations. Dozens of hips painted with conventional toxic antifouling paints can make a significant environmental impact in an enclosed harbor.

Since Navy operate both in US and foreign waters, compliance with Federal, State, local environmental regulations as well as with regulations imposed by the host countries is required to ensure unconstrained operation. To meet its needs, Navy has a strong commitment to develop and maintain environmentally sound/ship for the 21st century. The present proposal is a contribution to this effort with the goal of developing a toxic free coating that resists or reduces the attachment of marine fouling organisms. This proposal takes advantage of the weak adhesion characteristics of materials that have low surface free energies.

All marine fouling organisms use biopolymeric adhesive secretions for attachment. The strength of adhesion, expressed as the work of adhesion (the work required to separate the adhered liquid form the solid surface) (W_A) and the liquid (Y_1) minus the interfacial

tension (Y_{s1}) ($W_A = Y_s + Y_1 - Y_{s1}$, Dupre 1869). From this equation, it is clear that the lower the surface free energy of the solid (Y_s), the weaker the adhesion. Hull coatings with sufficiently low surface energy should prevent fouling because organisms would not be able to adhere to it.

The lowest surface free energies can be created by adsorbed monolayers of closely packed perfluorinated compounds. Since adsorbed monolayers are not practical as hull coatings, we propose to simulate them by grafting perfluoroalkyl compounds to surfaces, by embedding such molecules into the surface of polymeric matrices, and by binding the perfluorinated compounds into a polymeric backbone to create comb type polymers with perfluoroalkyl sidechains.

These types of polymeric materials have far lower surface free energies than Teflon and have promising properties for controlling biofouling. The key parameter is the molecular orientation at and immediately under the surface. Therefore, a major part of the proposed work will be dedicated to the elucidation of the molecular orientation of the various experimental systems. This knowledge will assist efforts in optimizing the orientation for minimum surface free energy and maximum performance as well as assessing the stability of the orientation in a seawater environment and the changes caused by the marine environment.

7. Project Description:

The specific objective of this project is to develop a nontoxic, zero discharge coating that protects ship-hulls from marine fouling organisms. Unlike conventional antifouling paints, such coatings will not contain toxic materials, rater they will be designed to resist fouling or allow only weak adhesion of fouling organisms. In order to minimize adhesion we will design materials with the lowest possible surface free energy. Our technical objectives are to: (1) Simulate adsorbed fluorinated monolayers either by grafting perfluoroalkyl molecules to surfaces, by embedding perfluoroalkyl compounds into the surface of polymeric matrices, or by synthesizing comb type polymers with perfluorinated side-chains for maximum effectiveness; (3) Determine the minimum amount of perfluorinated additive needed for optimum performance; (4) Reduce the amount of the expensive perfluorinated moiety by copolymerization of block-polymerization with non-fluorinated monomers to reduce cost; (5) Verify the effectiveness of the perfluorinated polymeric materials against the adhesion of marine fouling organisms.

Elucidation, control and stabilization of the surface orientation of the molecules and polymeric side-chains is a key technical issue. We will systematically optimize the curing and polymerization conditions to achieve consistent low surface free energies and antifouling/fouling-release properties. Additives and copolymerization are also important issues affecting surface property optimization and coat reduction. In addition to the surface free energy related measurements, the shear strength of a selected series of adhesives, including the mussel adhesive, will be determined. The adhesion strength will indicate the fouling release property of a polymeric surface.

Molecular modeling will help to verify and explain molecular orientations and interactions observed at the polymeric surface. We will use powerful computational chemistry programs such as Gaussian 92, SPARTAN and HyperChem on our Conter's Convex C3240 MiniSupercomputer. We will use computational chemistry to calculate surface free energies of model compounds, design low adhesion surfaces, and predict surface effects and molecular interactions at various interfaces.

Long-chain perfluorinated compounds will be prepared form a number of derivatives of perfluoroalkyl iodide homologues. These include acrylates and methacrylates for use as additives or for polymerization to form comb-polymers. Olefins prepared form the iodides will be hydrosilylated to form perfluoroalkylethyl silanes. The silanes are used to form self-assembled chemisorbed monolayers and polysiloxane comb-polymers. The iodides are also used to form perfluoroalkylethyl thiols which are grafted to metal surfaces, such as geld, to also form chemisorbed monolayers. Adsorbed and chemisorbed molecular layers of perfluoroalkyl compounds with various functional groups will serve as model surfaces to study molecular orientation and surface characteristics.

Various techniques will be used to determine the surface configurations of the fluorinated moieties. These techniques include grazing-angle infrared reflectance to calculate molecular orientation, X-ray Photoelectron Spectroscopy (XPS) to determine CF_2/CF_3 ratios on the surface, and visible light and infrared ellipsometry to measure film thicknesses. The molecular depth profile of the surface layer will be determined by variable angle Attenuated Total Reflectance methods. Depth-profiling provides information about the concentration distribution of perfluoroalkyl additives near the surface and also about the conformation of the polymer molecules and orientation of the side-chains at the surface and in the underlying layers.

We will simulate adsorbed molecular layers by mixing perfluorinated amphipathic compounds into uncured polymeric mixtures. The compounds chosen as additives include perfluoroalkyl acids, alcohols, amines, and esters. The additives migrate to the surface and the hydrophobic portion of the chains extrude from the matrix so that they ar e immobilized oriented at the polymer surface. The advantage of using additives is simple preparation that requires only small quantities of the expensive perfluoroalkyl compounds to achieve sufficiently low surface energies.

Comb-polymers will be synthesized form monomers with long perfluoroalkyl chains or by grafting perfluoroalkyl chains to existing polymeric backbones. These simulate adsorbed monolayers, producing surfaces with surface energies comparable to those of adsorbed molecular layers. In addition to the presently explored polymer system, the acrylates/methacrylates and the siloxanes, we will synthesize several new classes of polymers such as urethanes, epoxies and polyethylenes containing long perfluorinated side-chains. We will systematically determine the optimum factors that control the orientation of the perfluorinated moieties at the surface.

Parallel with this effort, basic research (6.1) on fluorinated poly-urethanes with low glass transition temperatures will be initiated at Naval Research Laboratory. The potential advantages of these polymers (1) Low surface energies; (2) Low glass transition

temperatures and high elasticity that may inhibit firm attachment of organism; (3) Low release energies that facilitates dislodging of the adherents; (4) Thermoplastic nature that simplifies waste disposal.

A recent development in oxetane chemistry has led to the synthesis of a new family of polyether glycols with fluorinated side-chains. urethanes based on these new macromers have been successfully prepared at NRL. Results from preliminary tests showed that these urethanes resist attachment of barnacles and preserve the surface properties after a long period of immersion in water.

The goals of the 6.1 part of research are: (1) Incorporate longer fluorinated side-chains into the polymers to reduce the surface energy; (2) Optimize composition and synthesis; (3) Understand the interactions between water and surface during long periods of contact and the relation to release energy.

A new family of fluorinated polyether glycols will be prepared by oxetane chemistry. Fluoroalkoxymehyl-3-methyl-oxetane (FOX) is obtained by reacting 3-bromomethyl-3-methyl-oxetane with fluorinated alkoxides in DMF at 70°C. Ring opening polymerization of FOX monomers is then conducted at 18°C using a lewis acid catalyst. The structure and length of the fluorinated branch can be varied for optimum performance. The fluorinated polyether glycol is reacted with diisocyanates and diols to form polyurethane. By varying the composition, the properties of polymer will be optimized.

The physical properties of the polymers, co-polymers and mixtures prepared both at NCCOSC/RDTE DIV and at NRL will be characterized and optimized for durability and low surface free energy. Low surface energy has been used as the primary design criterion for materials for fouling release. Recent work at NRL with dynamic contact angle analyzer (DCA) provides additional information for characterization . To keep a surface clean, low release energy is required to release the new adherents. A measurement of this release energy is the receding contact angle.

Nanoscale chemical composition and mechanical properties of polymeric materials can vary significantly either laterally or vertically. These variations can be characterized with X-ray photo-electron spectroscopy (XPS) and atomic force microscopy (AFM). It has been shown at NRL that nanoscale mechanical properties amy be quantitatively measured as a function of penetration depth using AFM as a nanoindentor. By obtaining a series of indentations and using a raster scan pattern across a surface, nanoscale three-dimensional mechanical property mapping may be performed on the sample surface. A recently developed algorithm which de-convolute results form XPS measurements can be used to perform corresponding chemical composition mapping. Structure-properties correlations in the surface region can be established.

The experimental coatings will be exposed to the marine environment to determine fouling resistance, fouling release, durability, and possible surface molecular changes caused by sea-water, biofilm and fouling organisms.

8. Expected Payoff:

Non-polluting, not-toxic antifouling coatings will be synthesized. This new antifoulant will have non-wetting low-energy surface which resists the attachment of the organisms. The low surface energy antifoulant releases no toxic material into the environment; therefore, no environmental hazard will be created. While toxic antifoulants are specific against certain types of fouling, the low energy surfaces prevent any kind of attachment and provide universal protection. More importantly, in the low surface energy coating; since its efficiency is based upon a physical surface phenomenon and not on depletive active substance, long effective lifetime is ensured. Both the Navy fleet and commercial shipping industry are potential users of the non-polluting fouling release coating.

9. Milestones:

1.	Synthesis of perfluoro compounds, including polyfluorooxetanes	03/94
2.	Polymerize (perfluoroalkyl) acrylates, siloxanes and urethanes	06/94
3.	Surface characterization, AFM, depth-profile, test and evaluation	08/94
4.	First Year Final Project Summary	11/94
5.	Optimize orientation of polyacrylates and polysiloxanes	01/95
6.	Synthesize copolymers	06/95
7.	Optimize perfluoro additives in polymeric matrix	06/95
8.	Test and evaluation	09/95
9.	Second Year Final Project Summary	11/95
10.	Optimize copolymers and block-polymers	01/96
11.	Determine the feasibility of surface grafting	06/96
12.	Test and evaluation	09/96
13.	Final Project Summary	11/96

10. Transition Plan:

After successful demonstration, the low-surface-energy non-polluting fouling-release coating will be transferred to suitable private companies (e.g. GenCore Polymer Division) as defense conversion for commercial scale production, and the fleet (NAVSEA) for implementation. Through the NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/biodegradable Antifouling Hull Coatings there is a high degree of coordination between performer and user.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	570	895	920	930	3315
NAVY	0	75	75	75	225
TOTAL	570	970	995	1005	3540

12. Performers:

The 6.2 portion of the project will be performed at NCCOSC/RDT&E Division Code 521, the 6.1 portion at NRL. The expertise of fluorochemical companies such as DuPont, 3M and GenCore Aerojet (Dr. Aslam Malik) will be recruited for synthesizing the necessary compounds and polymers. The development of the final coating will be performed with the cooperation of the paint companies (GenCore Polymer Division). Professor Joseph A. Gardella, Jr. of SUNY, Buffalo will be in charge of the XPS measurements. This project is coordinated with the ONR 6.1/6.2 Bimolecular Antifouling Program that includes developing and evaluating fouling release materials from industry, NRL and academic research. Also it will be coordinated with NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/Biodegradable Antifouling Hull Coatings that started in FY93 and will test and evaluate fouling release and biodegradable natural antifoulant coatings.

13. Principal Investigators:

Dr. Elek Lindner
NCCOSC/RDT&E Division Code 521
53475 Strothe Rd.
San Diego, CA 92152-6325
TEL: (619) 553-2795
FAX: (619) 553-6305

Co-Investigator:
Dr. Ann Mera
Naval Research Laboratory Code 6127
4555 Overlook Ave SW.
Washington DC 20375-5320
TEL: (202) 404-8893
FAX: (202) 767-0594

14. Keywords:

antifouling paints, coatings, low surface energy, non-polluting, perfluoroalkyl, fluorinated polyurethane, oxetane, minimally adhesive surfaces, release energy, receding contact angle, nanoscale surface mapping

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Organic Protective Coatings and Application Technology

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division - Warminster

5. **Proposal ID:** #065

6. Problem Statement:

To develop high performance, non-toxic, low volatile organic compounds (VOC) content coatings for Navy use. Organic coatings are the primary source of protection against environmental degradation for Navy aircraft (A/C), weapon systems and ground support equipment (GSE). In addition, these materials provide passive countermeasures against many enemy threats. There are a large number of different coating systems currently used by the Navy due to the diverse nature of their functions; the variety of substrates & alloys to which they are applied; and the severe nature of their operational environment. These protective coatings contain toxic inhibitors (i.e. lead, chromates, etc) and high VOC contents. These components are released during painting operations as organic and toxic air emissions. Federal, state and local environmental agencies like the EPA and California Air Quality Management Districts (AQMD) classify these materials as hazardous and restrict their emissions through regulations such as the Clean Air Act, Clean Water Act, CERCLA, Resource Conservation and Recovery Act (RCRA) as well as local EPA and AQMD rules. In addition, OPNAV and CNO directives require significant reductions in the amount of hazardous waste generated by the Navy. Finally, painting operations at maintenance depots are a major contributor to hazardous material and waste generation in the DoD. Therefore, it is necessary to develop new high performance coatings that meet current and future environmental restrictions while allowing the Navy to continue painting operations. This effort is covered under the Tri-service EQ Strategic Plan Area: Pillar 3: Pollution Prevention, Requirement Thrust: 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

7. Project Description:

A full spectrum approach for reducing the VOC and air toxic emissions from protective coatings will be pursued. To begin with, investigation in low VOC polymer technology will be used to produce low VOC binder systems. Reactive monomers/oligomers and diluents will be developed to obtain low viscosity, low VOC binder systems for future organic coatings. In addition, recent advances in water-borne resin technology will allow for the development of high performance water-borne topcoats which are compliant with these regulations. Coating corrosion

resistance, physical performance properties and VOC content will be evaluated to develop the best materials. Furthermore low/no VOC protective coatings (such as electrocoatings, powder coatings, bearing adhesives, fuel cell repair, NDI penetrants, etc) will be investigated for potential aerospace applications. Several recently developed VOC compliant, non-toxic alternative materials will be investigated for this program. These compliant coating systems include Unicoat (a non-lead, non-chromate, low VOC self-priming topcoat); compliant lacquer topcoats and non-toxic inhibitor systems. The non-toxic inhibitor systems will be used to develop replacements for the current lead and chromate containing materials. These materials will be optimized, service evaluated and implemented for Navy use. Finally, conventional air spray equipment used to apply these materials, has a transfer efficiency of only about 28%. Therefore, implementing high transfer efficient spray equipment would significantly reduce the amount of air emissions from painting operations. Application equipment such as air-assisted airless, electrostatic, and high volume low pressure (HVLP) will be evaluated.

8. Expected Payoff:

The development of non-toxic, VOC compliant coatings will enable the Navy to meet current and future environmental regulations as well as reduce the total amount of hazardous waste the Navy generates. In addition, these new materials will eliminate the need for the installation of extremely expensive control equipment (i.e. $1-5M per spray booth for VOC emission control). This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and disposal costs, Navy A/C and equipment operational readiness will be maintained by using these new coatings. This is particularly important considering the cost of these A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to many areas of the commercial sector (aerospace, automotive, marine, etc).

9. Milestones:

1.	Develop Compliant Lacquer Topcoats	09/91
2.	Characterize Non-Toxic Inhibitors for Organic Coatings	09/91
3.	Service Demonstration of Unicoat - Self-Priming Topcoat	06/92
4.	Develop Non-Toxic Inhibited Organic Coatings	09/92
5.	Optimize Compliant Lacquer Topcoats	09/92
6.	Test High Transfer Efficiency Application Equipment	12/92
7.	Implement Unicoat - Self-Priming Topcoat	02/93
8.	Service Demonstration of Compliant Lacquer Topcoats	09/93
9.	Develop Water-Borne Topcoats	09/93
10.	Optimize Non-Toxic Inhibited Organic Coatings	12/93
11.	Optimize High Transfer Efficiency Application Equipment	12/93
12.	Investigate Low VOC Polymers for A/C Coatings	12/93
13.	Optimize Water-Borne Topcoats	06/94
14.	Implement Compliant Lacquer Topcoats	06/94
15.	Service Demo of Non-Toxic Inhibited Organic Coatings	07/94

16.	Implement High Transfer Efficiency Application Equipment	09/94
17.	Develop A/C Coatings Based on Low VOC Polymers	09/94
18	Investigate Compliant NDI Penetrants	12/94
19.	Implement Non-Toxic Inhibited Organic Coatings	07/95
20.	Optimize Low VOC Polymer Coatings	09/95
21.	Service Demonstration of Optimum Water-Borne Coatings	09/95
22.	Develop Powder Coatings for A/C Applications	10/95
23.	Develop Electrocoatings for A/C Applications	10/95
24.	Test Use of Supercritical CO_2 as an A/C Coating Diluent	12/95
25.	Optimize Compliant NDI Penetrants	12/95
26.	Implement Water-Borne Topcoats	03/96
27.	Service Demo of Optimized Low VOC Polymer Coatings	06/96
28.	Optimize Powder Coatings for A/C Applications	09/96
29.	Optimize Electrocoatings for A/C Applications	09/96
30.	Optimize Supercritical CO_2 as a Coating Diluent	10/96
31.	Service Demonstration of Compliant NDI Penetrants	12/96
32.	Implement Optimized Low VOC Polymer Coatings	09/97
33.	Service Demo of Powder Coatings	09/97
34.	Service Demo of Electrocoatings	09/97
35.	Service Demo of Supercritical CO_2 as a Coating Diluent	09/97
36.	Develop/Optimize Non-VOC Fuel Cell Repair	09/97
37.	Develop/Optimize Non-VOC Bearing Adhesives	09/97
38.	Implement Compliant NDI Penetrants	09/97
39.	Implement Powder Coatings	09/98
40.	Implement Electrocoatings	09/98
41.	Implement Supercritical CO_2 as a Coating Diluent	09/98
42.	Service Demonstration of Non-VOC Fuel Cell Repair	09/98
43.	Service Demonstration of Non-VOC Bearing Adhesives	09/98
44.	Implement Non-VOC Fuel Cell Repair	09/99
45.	Implement Non-VOC Bearing Adhesives	09/99

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through the Lead Maintenance Technology Center for Environment. Following demonstration, they will be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	400	550	930	855	610	470	3415

12. Performers:

Development of non-toxic, low VOC protective coatings is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. These efforts are being coordinated with resin/coatings industry (Miles Inc, Air Products, Deft, BASF, Spraylat Courtaulds, etc), Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), Army (ARL, etc), equipment manufacturers (Graco, Binks, etc) and aerospace industry (MDA-E, Boeing, Rohr, etc.).

13. Principal Investigator:

Stephen J. Spadafora
Naval Air Warfare Center Aircraft Division Warminster
P.O. Box 5156 (Code 6062E)
Warminster, PA 18974-0591
Phone: (215) 441-2704
FAX: (215) 441-1925

14. Keywords:

Organic Coatings, Materials Substitution, Paint Application Equipment, Low VOC Polymers, Volatile Organic Compounds, Non Chrome/Lead coatings

SERDP FY94 PROPOSAL

1. SERDP Thrust Area: Pollution Prevention

2. Title: Integrated Expert Solvent Substitution Data Base

3. Agency: EPA, Office of Environmental Engineering and Technology Demonstration

4. Laboratory: HQ and AEERL

5. Proposal ID: #331

6. Problem Statement:

The goal of this project is to build an integrated solvents substitutes data base from existing data bases and potentially redundant activities underway in each of the participating and other agencies. The resultant expert tool would combine priority information from each existing data base such as compatibilities and performance, and fill gaps by providing economic analyses and vendors information. It would be targeted for direct use by all DoD depots, logistics centers, defense contractors, small and medium industries as well as State Technical assistance offices, NIST Manufacturing and Technology Centers, and universities implementing the EADS program. This data base could provide an important technology transfer function for Federal Agencies, states, and small and medium industries to advance the reduction of hazardous waste releases/emissions in meeting the Executive Order on Federal Compliance's (12856) 50% reduction of TRI toxics by 1999, and the Clean Air Act/SNAP hammer deadlines. It will assist in the redevelopment of many Mil Spec Standards under executive Order 12856, and will assist each agency and the US in meeting its ozone depletion reduction, and toxics use reduction goals. The project will also demonstrate federal cooperation and environmental leadership by promoting and making publicly available the successes and lessons learned by the participating agencies.

7. Project Description:

Develop an integrated expert solvent substitutes data base that will combine related data base efforts across agencies and expand those efforts in depth and breadth. Objectives would include targeting related solvent data base tools for integration; develop expert front end for expanded PIES solvent umbrella; integrate compatible platforms, conduct research and develop system architecture for non-compatible platforms; develop strategy for the testing of new alternatives; validate that information through existing test bed centers; conduct deployment/feedback program.

This proposal is strengthened by the full life cycle design of the expert tool including deployment by State Technical Assistance Centers and update/expansion through

generation of new alternatives through its own research testing and validation program, and a self expanding industrial feedback loop. The tasks of this project will be closely guided and prioritized by a technical review board comprised of participating agencies, labs, test bed facilities, industry and State P2 Technical Assistance Programs.

This project promotes the SERDP objective of maximum exchange of information via several deployment mechanisms. It is designed to assist government agencies and industry as an information exchange data base to be linked with the PIES, DENIX, EPIC, and LINKS networks over INTERNET for widespread electronic access. This array of electronic dissemination of DoD and DOE solvent alternatives knowledge and leadership meets a second objective of SERDP, to provide appropriate access (to federal, state, and local governments and industry) to data available to DoD and DOE relevant to environmental matters. The National Center for Manufacturing Sciences and the National Roundtable of State Pollution Prevention Programs are committed to networking the final product throughout their membership. The Roundtable, NIST MTC's, and the academic institutions of the EADS program represent a massive hands-on deployment mechanism. More than 70 technical assistance centers operated by these programs will use the tool in on-site assessment visits to industries within their jurisdictions.

This project implements a third objective of SERDP by minimizing the duplication of environmentally related research. The purpose of this project is to integrate similar solvent substitute data bases and focus on growth of the integrated tool through a coordinated, monitored effort by representatives of a technical review board. This project will further coordinate alternatives being validated at a number of existing test centers. Participation of these centers in the validation portion of this project will promote coordination of activities at these centers. We intend to use the following test bed centers for the validation function of this project: DoD's National Defense Center for Environmental Excellence (NDCEE); DOE's Idaho National Engineering Laboratory; University of Tennessee's Center for Industrial Services; and the Illinois Hazardous Waste Resource Information Center. Other validation test bed facilities will be considered for inclusion.

This project meets a fourth objective of SERDP, by spurring three tiers of development and demonstration activities. These three tiers include research and development to design a system architecture for non-compatible data base tools; the development of an expansion strategy that will operate a testing regime to generate new data for the integrated data base; and the implementation of a validation program which will use existing test bed centers (as neutral third parties) to verify the utility of new substitutes or process alterations.

By deploying this expert data base through the depots and logistics centers, national labs, State, NIST and EADS technical assistance centers we are providing governmental and nongovernmental entities with analytical assistance in reducing toxics use and meeting the bans of ozone depleting substances under the Clean Air Act the Montreal Protocol, and Executive Order 12856. We are therefore meeting a fifth objective of SERDP, providing analytical assistance in reducing military and

industrial ODS impact on the stratospheric ozone layer. This objective will be met by networking this expert tool throughout all service bases and joint depot maintenance shops. More massive impacts will be seen with widespread application of the tool to the small and medium businesses of the plating, fabrication, electronics and maintenance and repair industries.

The project will build on the EPA's Solvent Alternatives Guide (SAGE), and PIES Vendor data bases; DOE/INEL's HSSDS and SHSD databases; the National Center for Manufacturing Sciences (NCMS) Solvent and Materials Compatibility data bases; and others as identified. Ultimately the system will be comprised of a fully integrated data base that builds on aspects of SAGE to assist users in identifying alternative technologies and chemical groups based on their knowledge of the application. The system will be supported by compatibility and chemical test data (from INEL HSSDS, SHDS, and NCMS) to assist users in identifying suitable replacement chemicals/technologies for their application; vendor information (from PIES and NCMS) to identify sources for alternatives; and case study information (from PIES) to provide information on effectiveness, payback and potential problems with the alternative selected. The data base developed under this project will focus exclusively on solvents and will serve as a model for subsequent expansion efforts to address other industrial sector applications.

The project will enhance the technology transfer work of the PIES expansion project under SERDP in 1993 where information umbrellas are established within the P2 network, as well as on the GUI programming research initiated under that project.

Project Tasks: The tasks involved in this project encompass:
I. Establish a Technical Advisory Board/User group: This board, representing participating Agencies and targeted users, will guide each stage of this project. It will set the priorities in the testing and validation phases, design requirements of the final system, and beta test various project accomplishments.
II. Identify information sources and relationships: This task will involve an exhaustive search to identify other data bases that should be considered in the integration. This task will evaluate: function; data gaps; relationships between data bases; areas of duplication; and data formats and file structures.
III. Expand the PIES information umbrella: This builds on FY93 SERDP funding which establishes information umbrellas pointing to several tools under a single network. These will be expanded to house other solvent systems from federal and private sectors.
IV. Create an expert front end and integrate compatible tools: Compatible systems will be integrated and combined. This will reduce duplication of information and provide a seamless, integrated data environment. The user will be able to navigate easily through several tools without the need to learn separate operating command structures.
V. Develop system architecture for non-compatible platforms: Those systems having incompatible data structures will be integrated into the system. A system architecture that can access the differing systems based on the previously implemented intelligent front end will be developed to provide seamless, intelligent access to all the information available.

VI. Generate new information: The technical advisory board will develop a strategy to initiate testing and research of new alternate technologies and substitutes. This strategy shall combine chemical reduction, process, and regulatory hammer priorities. Test bed centers such as the NDCEE, INEL and the University of Tennessee shall be used for testing.

VII. Establish continuous feedback loop including site visits by State TAPs: State technical assistance centers will determine what substitutes were made as a result of using the tool. This will be added into the data base as an implementing user resource. NCMS will assist workshops directed at supplier networks with participation of United Technologies and Texas Instruments.

VIII. Deployment/marketing/training: The system will be deployed using the Depot/logistics centers, State Technical Assistance Programs, NIST MTC's and the EADS universities in their on-site industry assessments. EPA and States will directly network with local Chambers of Commerce. Use of INTERNET for access to PIES/DENIX/EPIC integrated solvents tool will promote further interface with the National Information Infrastructure including Enterprise Integration Net, Product Data Exchange Standards, CALS, and others.

8. Expected Payoff:

The benefits of this effort for DoD, DOE, and EPA include better centralized access to pertinent information to reduce the use of toxic and ozone depleting solvents; and a reduction of redundant research efforts. The benefits to industry include easier access to technical information that will allow them to implement alternatives and reduce the emissions of ODS and other toxics; and assist in meeting the bans under the Clean Air Act. Industrial benefits include monetary savings and liability reduction due to implementing P2 alternatives. The project will provide a measurable indicator of its impact on industrial facilities in terms of cost savings and ODS reduction gained through options implemented.

9. Milestones:

1.	Establish technical advisory board	5/94
2.	Create GUI/Mosaic platform for PIES	8/94
3.	Identify information sources/relationships/gaps	9/94, 9/96
4.	Expand PIES/DENIX/EPIC solvent information umbrella	10/94
5.	Generate new info via board strategy; quarterly adds	11/94
6.	Expand Umbrella to include other Fed. dbs	6/95
7.	Develop Expert system for solvent info synthesis	9/95
8.	Initiate validation testing & industrial feedback loop	1/96
9.	Initiate State/NIST/MTC TAP deployment & implemented feedback	1/96
10.	Augment State TAP training based on system progress	9/96, 5/97
11.	Conduct testing & validation for generation of new information throughout project	1/95-9/97
12.	Conduct on-site verification as feedback mechanism throughout project	9/97

10. Transition Plan:

The expert system will be accessed by industrial users directly through Internet. Also, the State TAPs, NIST MTCs, and the universities implementing DOEs EADS Program, will network the system through their on-site P2 assessment visits. Industrial access will also be gained through a direct networking/training effort for local Chambers of Commerce and Trade Associations.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	3000	2400	2300	0	8600

12. Performers:

DoD: Navy: Naval Facilities Engineering Service Center, Larry Hill. Army: Corps of Engineers, Defense Environmental Corporate Information Management Program Office (DECIM), Connie Watts. Air force: Center for Environmental Excellence Brooks AFB, Steve Green. National Defense Center for Environmental Excellence, Jack Adams. DOE: ER Arnold Edleman. INEL: Kevin Twitchel. NIST/MEP: Dave Gold, EPA: AEERL, Charles Darvin. Nat. Cent. for Man. Sciences, Mike Wixom. Univ. Tenn: George Smelcer; WRRC: Vic Young.

13. Principal Investigator:

Myles Morse
US EPA
Office of Research and Development
Office of Environmental Engineering and Technology Demonstration
401 M Street, S.W.
Washington, DC 20460
TEL: (202) 260-3161
FAX: (202) 260-3861

14. Keywords:

solvent; network; ODS; P2; compatibility; vendors

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Rapid Testing for Acceptable Materials and Processes

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center

5. **Proposal ID:** #117

6. Problem Statement:

The goal of this project is to develop low risk, fast track methodologies and techniques for military qualification of new or modified environmentally benign materials.

Continuing efforts to develop environmentally acceptable materials and processes are constrained by the time-consuming process of qualification testing. Users (customers) must make their decision under conditions of uncertainty and want to take as low as risk possible in the decision. Frequently, substantial testing was conducted in support of the initial product qualification decision or in support of re-qualification for design modification to improve performance or solve problems. The present qualification test process is both time consuming and costly and is often preempted by environmental compliance or enforcement requirements.

There is a real need to develop accelerated and less costly means for qualification testing of alternate, substitute and emerging new materials and processes in order to rapidly introduce environmentally acceptable materials into the military inventory and force structure. Economical means are required in order to preserve a diminishing source base threatened due to costly restrictions.

This is a FY93 Funded SERDP Project requiring FY94 Continuation.

7. Project Description:

The objective of this project is to create combined environmental and reliability test techniques with 20:1 time compression ratio in areas such as corrosion, sonic and low-cycle fatigue, adhesive delamination, canopy deterioration, paint aging, and plastic embrittlement.

An integrated product development (IPD) team will be created to conduct a systems engineering analysis of qualification test requirements and provide focus on where material science and research efforts are required. The IPD team will be composed of representatives of Wright Laboratory Materials Directorate, Flight Dynamics Directorate, Propulsion Directorate, Aeronautical Systems Center Systems Engineering

Directorate, Air Logistics Center maintenance engineering, and selected representatives from the material supplier base.

Phase I will identify and prioritize materials and processes requiring costly long lead qualification testing requirements such as corrosion, sonic fatigue, and low cycle fatigue.

Phase II will characterize material aging physics and develop the theoretical bridge between real life testing and accelerated testing on selected characteristics and phenomena.

Phase III will formulate methodologies and present technique design concepts to conduct accelerated testing using advanced techniques, assemble historical life testing results in selected material technology areas, and conduct a limited number of accelerated tests to demonstrate the feasibility and viability of the concepts and correlate results with traditional methods.

There are no known comprehensive efforts previously accomplished in this specific research area.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes.

The project will provide a method of accelerating qualification of a large number of technology development projects involving development of alternates and substitutes for materials with hazardous or toxic manufacturing wastes.

Tasks/Activities

(1) Select high leverage materials -- those being driven by or forced by legislation
(2) Characterize time dependent failure modes and test requirements:
(3) Characterize test modes (fatigue, vibration, corrosion)
(4) Examine assumptions and rationale behind testing requirements and techniques
(5) Build theoretical bridge
(6) Identify most promising acceleration testing methodologies
(7) Compare and correlate accelerated testing results using traditional materials with those obtained with those using traditional methods (from historical records and qualification test reports)
(8) Initiate accelerated testing for environmentally benign alternate and substitute materials.
(9) Link with information sources such as the Government/Industry Data Exchange Program (GIDEP) and the USEPA Pollution Prevention Information Exchange System (PPIES) to exchange qualification test results among programs and assess impacts to military specifications and standards

The major technical issues to overcome relate to:

(1) Acceleration physics and
(2) The degree of empirical evidence required to support configuration change decisions

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.J
Requirements Category:	3.III.2.f
Work effort:	Tech Base

8. Expected Payoff:

Potential users include aerospace manufacturers (especially those manufacturing dual use civilian/military products), Air Logistics Centers, Integrated Weapon System Program Offices, and DoD industrial operations. Professional societies such as American Society for Testing Materials (ASTM) will be invited to participate in reviewing project plans, progress, and results. The development of an acceptable accelerated testing technology will reduce time for testing, reduce testing cost of testing, and eliminate costs of environmental compliance and hazardous materials//waste management. These efficiencies and economies will result from elimination of unnecessary or redundant tests and earlier implementation of clean technology.

9. Milestones:

1.	Initiate Project Begin studies to select target materials and testing requirements	03/93
2.	Target materials and tests isolated	06/93
3.	Contract award Initiate studies of failure modes and test modes	08/93
4.	Failure modes identified Test modes identified	09/93
5.	Aging physics identified	03/94
6.	Theoretical bridge established	05/94
7.	Peer review	06/94
8.	Advanced testing techniques selected	08/94
9.	Initiate ATTD/Manufacturing Technology planning as required	12/94
10.	Demonstration of advanced techniques and correlation of test results with historic data	08/95
11.	Technology transfer media released	09/95

10. Transition Plan:

Users will be participants on the IPD team for needs validation, priority setting, methodology approval, and review of demonstration results.

11. **Funding:** ($K)

	FY93	FY94	FY95	TOTAL
SERDP	100	263	262	625

12. **Performers:**

The project will be performed under the technical leadership and direction of:

Air Force Material Command
Aeronautical Systems Center
Wright Laboratory
Materials Directorate
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

13. **Principal Investigator:**

Jim Mazza
WL/MLSE
Wright-Patterson, AFB OH 45433-6703
TEL: (513) 255-3691
FAX: (513) 476-4419

Wright Laboratory has extensive Research and Development experience in the area of correlation of laboratory testing of materials and processes with qualification and service testing.

14. **Keywords:**

Qualification testing, Age testing, Corrosion, Fatigue testing

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Life Cycle Engineering & Design Program

3. **Agency:** EPA

4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)

5. **Proposal ID:** #304

6. **Problem Statement:**

Over the past several years, DoD, DOE and EPA have undertaken independent and joint efforts to develop pollution preventing techniques and technologies for implementation at Federal facilities. Key areas of concern have been addressed through RD&D in on painting and depainting, cleaning and degreasing, ozone depleting chemicals, metal fabrication and finishing.

Life Cycle Assessment, Analysis and Design (LCA) is being viewed as the preferred tool for analyzing an operation, system, or activity and designing environmentally benign processes into the base engineering. LCA differs from previous approaches in that it views all resource, energy and cost inputs to a product (inventory analysis), as well as all the associated waste streams (impact analysis), and evaluates and implements opportunities to reduce environmental burdens (improvement analysis) from cradle to grave. This approach is based on the product life cycle, which includes raw material acquisition and processing, manufacturing, use/service, resource recovery and disposal.

The LCA tool meets the SERDP RD&D goal to "address matters of concern to unencumber military operations, enhance military systems' effectiveness, and improve the safety of personnel in meeting the Departments' environmental obligations." Only through the application of a cradle to grave analysis and engineering design approach in the development of military systems can the DoD be assured that a specified system is operating effectively with minimal environmental impacts. Because the projects selected involve technologies with broad applications in public and private sectors, this proposal also supports the SERDP goal to, "help solve significant national and international environmental problems through the application of the Departments' technical capabilities, analytical systems and information."

LCA design emphasizes integrating environmental requirements into the earliest phases of design and successfully balancing these requirements with all other necessary performance, cost, cultural, and legal criteria. Under the Pollution Prevention Thrust Area, LCA design will enable DoD/DOE/EPA to meet SERDP research and development objectives in (1) the development of non-hazardous alternate defense

unique paints (e.g., CARC), (2) development of cost effective and non-polluting improved industrial processes and low VOC substitute chemicals for depainting, and (3) the development of predictive models and methodology to aid in the development of environmentally sound weapon systems throughout their life cycle and decommissioning

The Life Cycle Engineering & Design Program will develop projects (identified below) that meet the research category descriptions of applied research and technology demonstration. Technology transfer may be accomplished within the cooperating departments and agencies or through the WREAFS program (Waste Reduction Evaluations at Federal Sites). The WREAFS program is designed to provide technical assistance and support to Federal facilities in conducting pollution prevention research. While the Life Cycle Engineering & Design Program is a new effort, it will build upon LCA methodology and development work already laid down in RREL's LCA, Clean Products and Clean Technologies programs.

7. Project Description:

The thrust of this program will be to take selected innovative technologies and products, applying LCA design analysis to them to determine the net environmental and cost burdens. The LCA will apply methodology and design techniques previously developed under RREL's programs. In FY94, the Life Cycle Engineering & Design Program will develop three LCA design projects:

Project #1 -- MEK Substitute in Aircraft Radome Depainting

Under the WREAFS program, RREL has researched and evaluated substitutes for methyl ethyl ketone (MEK) as cleaners and solvents in aircraft maintenance operations at Tinker Air Logistics Center (ALC) in Oklahoma. Tinker ALC performs maintenance, including structural repair and re-fabrication of USAF aircraft, notably the B-1B and the B-52. Tinker ALC reported using MEK at an annual rate of 5,385 gallons to wipe-down aircraft, and 8,250 gallons to depaint aircraft radomes.

From its research and in cooperation with Texaco, RREL identified solvent formulations based on propylene carbonate and n-methyl pyrrolidone as possible alternatives for MEK. The test focused on the ability of the chemical mixture to accomplish the job required, and meet the same MILSPEC standard as MEK without modifying the operational procedures.

This study determined that a blend of 25% propylene carbonate, 50% n-methyl pyrrolidone and 25% Dibasic ester (PC blend) removed paint in comparable time to the MEK. Hardness tests showed that the PC blend did not embrittle the fiberglass/epoxy substrate of the radome, nor did it effect flexural properties. Scanning with electron microscope indicated no significant damage to the fibers or fiber matrix interface. Test samples were successfully re-painted and demonstrated complete paint adhesion. For solvent properties, the PC blend compares favorably

with MEK. The PC blend has a flash point of 210OF (against MEK's 20OF), low toxicity, and lower evaporation rate.

The Life Cycle Engineering & Design Program will evaluate this new formulation in an LCA approach that investigates the energy and environmental impacts of the product as well as the engineering design of the system in which it is used. Methodology laid down in RREL's manual, "Life Cycle Assessment: Inventory Guidelines and Principles," will be applied. The first step will be to conduct an inventory analysis on depainting operations, and the PC Blend, to determine the resources used and actual environmental releases. An impact analysis will determine all the environmental consequences associated with depainting, including the production, use, and disposal of the PC Blend and potential contaminants from the depainting operations. The improvement analysis will focus on evaluating environmental consequences, the PC Blend, other potential alternatives, and MEK. Inherent in this approach will be the standard of meeting mission requirements (e.g., MILSPEC standards and technical order requirements.

In its recently published, "Life Cycle Design Guidance Manual," RREL demonstrates a systems-oriented approach to minimizing environmental impacts and risks via LCA. LCA design includes the application of such concepts as concurrent design, total quality management and cross-disciplinary teams. LCA design principles will be applied to this project to ensure the development of an ecologically and economically sustainable depainting system that fulfills performance requirements.

Project #2 - Improved Chemical Agent Resistant Coating (CARC) Applications Ft. Eustis, Virginia, has completed a base-wide pollution prevention program plan, and has supported previous WREAFS assessments and related studies on-site. During the course of this work, Ft. Eustis identified a need to significantly improve CARC painting and depainting operations, moving to upgrade depainting operations with alumina silicate, separating and recycling grit, and acquiring high-volume, low-pressure (HVLP) painting equipment.

Having made individual upgrades in operations, Ft. Eustis provides the opportunity to conduct an in depth evaluation of CARC painting operations at a typical base painting facility. There are several potential opportunities to test and implement techniques for improved transfer efficiency systems, and integrate them together in a common package designed to meet an individual facility's needs. The purpose of this project will be to conduct an LCA of Ft. Eustis painting and depainting operations, beginning with an inventory analysis of CARC painting and depainting operations to determine the resources used and environmental releases. An impact analysis will determine all the environmental consequences associated with CARC operations, including corrosion control techniques. By evaluating the environmental consequences, the improvement analysis will identify improvement opportunities which will be implemented and evaluated on-site.

As with the previous project, LCA design principles shall be applied to maintain focus on aggregate environmental impact reduction while ensuring performance criteria are

fully met. All potential areas of opportunity, from system design to operating procedures and practices, shall be evaluated. For example, because an opened container of CARC cannot be re-sealed and stored, its unused contents must be disposed of properly. One of the objectives of this study will be to design and test a technique to eliminate that waste.

Project #3 -- DOE Complex-wide LCA Design Case Studies

DOE has depended extensively on the use of process waste assessments in evaluating their technologies and identifying areas of possible environmental improvement. In the area of design and development of weapon systems and the related critical weapon components, the life cycle concept can identify existing or potential environmental problems that may be caused anywhere within the product system, from well head to final disposal. One specific component of particular interest and in which activity has already been started in LCA is related to the Gas Transfer System (GTS), a weapon component currently in production at Rocky Flats, Pinellas, and Savannah River. The purpose of this project is the incorporation of LCA methodology into a major Sandia design group and provide a model for future use leading to the widespread application to other DOE design agencies.

Another area of interest in which DOE/SNL has began activity relates to total cost assessment (TCA). TCA also incorporates the entire life cycle of a product or process but it focuses on internal and external costs that may be incurred. While LCA provides a range of information to support environmental decision-making, cost information has not typically been integrated with LCA environmental release data. Integration of cost data into the LCA approach will enhance its utility as a decision support tool.

This project builds on a current DOE funded project which is developing a technical framework, called Life Cycle Cost Assessment (LCCA), for conducting life cycle cost assessments. This project will take the framework to the next phase of demonstration allowing for further development and refinement.

8. Expected Payoff:

An overriding benefit from all projects would be in the testing and customizing of LCA design approaches for DoD applications, as each project would provide lessons learned in using LCA tools for environmental risk reduction. For each of the three selected projects, the following payoffs are expected:

Project #1 -- MEK Substitute in Aircraft Radome Depainting

The anticipated benefits include the elimination of a 33/50 toxic chemical, MEK, from the radome depainting operation, along with the VOC air emissions. The WREAFS evaluation of the PC Blend demonstrated a $30,085 annual savings over MEK usage. We expect broad technology/product transfer opportunities across DoD operations. Follow-on projects would focus on depainting/painting characteristics of a PC blend

and alternatives for a variety of thermoplastic and thermoset resins as their use is expanded in aircraft manufacturing.

Project #2 - Improved Chemical Agent Resistant Coating (CARC) Applications Ft. Eustis, Virginia. While CARC material is undergoing tests and reformulation to reduce VOC content and additional research is contemplated, there is an urgent need to address the operational applications of CARC as it is currently available. The model approach proposed here will generate guidance with applicability to facility CARC painting operations throughout the Army and DoD-wide. Costs will be tracked and the payback period will be proven in the implementation. It is anticipated that, through source reduction, more paint will meet the truck, and less will go in the can, generating cost savings and increasing operational efficiency. Lessons learned here will have application to all DoD CARC applications (e.g., vehicles, armor, weaponry, rotorcraft, etc.) in Army, Navy/Marine, and Air Force facilities. EPA's WREAFS program will provide additional support in evaluating the potential for application of lessons learned to marine anti-fouling paints and coatings.

Project #3 -- DOE Complex-wide LCA Design Case Studies

The largest payoff will be the avoidance of future environmental problems as new or next generation products are developed. This has been seen in various weapon systems which were designed for a specific use but have outlived their usefulness and are now not easily disposed of for various regulatory reasons. These weapons require expensive maintenance until a solution for disposal can be found. This type of problem may have been avoided if the designers had considered end-of-life issues during the development of the product.

9. Milestones:

1.	Collect and Compile Data	12/93
2.	Develop LCA Approach and Preliminary Research Plan	01/94
3.	Identify Alternative Materials and Engineering Designs	05/94
4.	Define Life Cycle of Project Operations and Refine Plan	07/94
5.	Report Findings and Final Research Plan	09/94
6.	Select Technologies/Products for Evaluation	12/94
7.	Conduct On-site LCA Evaluations of Selected Technology(s)	03/95
8.	Report Evaluations	08/95
9.	Refine and Implement Design Upgrades / Alternative Materials	11/95
10.	Evaluate Implementation	06/96

10. Transition Plan:

Technology and information will be transferred through a number of vehicles. EPA and the WREAFS program transfers information through industry contacts and panels, electronic bulletin boards and clearinghouses such as PPIC, the National Technical Information Service (NTIS) and Office of Research and Development mailing lists and networks. With Ft. Eustis being a member of the Tidewater

Interagency Pollution Prevention Program (TIPPP), its projects have an added visibility and opportunity for transfer across DoD. Some projects, such as the MEK substitution, shall benefit via CRADAs with industry. Air Force organizations such as AFCEE and AFIT shall participate in technology transfer. Also, DOE networks shall be accessed as appropriate.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	750	400	300	300	1750
EPA	200	200	200	200	800
TOTAL	950	600	500	500	2550

12. Performers:

Tinker Air Logistics Center, U.S. Air Force, with Thomas Walker as point of contact, and Texaco Corp. via CRADA agreement shall participate in the MEK replacement (PC Blend) study. Ft. Eustis Army Transportation Command, with Helen Turner as the point of contact, shall participate in the CARC project. And both Sandia National Laboratory and Los Alamos National Laboratory, with Ker Chi Chang as the point of contact, shall support the DOE project.

13. Principal Investigator:

Kenneth R. Stone
USEPA/RREL
Cincinnati, OH 45268
TEL: (513) 569-7474
FAX: (513) 569-7111

14. Keywords:

MEK, painting, depainting, solvents, computer modeling, LCA

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Model for Facilities Life Cycle Decisions

3. **Agency:** US Environmental Protection Agency

4. **Laboratory:** Air and Energy Engineering Research Laboratory

5. **Proposal ID:** #307

6. **Problem Statement:**

Goal: The goal of this project is to develop and field test a knowledge-based model of environmental characteristics/attributes to support the decision processes involved in facility design, construction, and operation.

Background: Decisions (i.e., design, construction, operation and renovations, and demolition) are made throughout a facility's life cycle which are based primarily on economic and in-place performance. Environmental factors (e.g.,energy and resource use, toxic by-products, indoor air quality, waste products, etc.,) are not considered in any of the current technical, pricing, or planning data used as the basis for these decision. The inclusion of environmental factors are essential in optimizing the standard facility decision processes, obtaining the maximum benefits from limited natural and economic resources, and reducing the potential for adverse environmental impacts.

This project is a continuation of a SERDP project initially funded in FY93.

As such, it is enhancement of an existing US Army's Corp of Engineers' Construction Research Laboratories (CERL) Small Business Innovative Research effort to test the feasibility of a Knowledge-Based Model which combines environmental and the standard facility decision factors. The initial prototype advisor incorporated inputs from AEERL's work with the American Institute of Architects. CERL FY92 funds for the prototype totaled $50K. The demonstration of the prototype was successful and co-funding in FY93 and FY94 from the Corp of Engineers has been authorized.

7. **Project Description:**

Previous Efforts: The US Army's Corp of Engineers' Construction Research Laboratories (CERL) are currently exploring the feasibility of a Knowledge-based Model that will enable the consideration of environmental factors during the various phases of a facility's life. In addition, CERL performs research to improve and optimize the various components (e.g., costs, system performance, etc.) of facility construction and operations and to improve construction productivity.

AEERL's Indoor Air Branch (IAB) is involved in research to characterize indoor emission sources and methods of mitigating indoor air quality (IAQ) impacts. IAB has a cooperative agreement with the American Institute of Architects (AIA) to develop environmental life cycle data for materials used in construction. IAB is finalizing a set of catalogs on indoor air emissions sources which assigns SIC Codes, MasterSpec Codes, chemical constituent, and chemical emissions data to those materials typically found in indoor environments. IAB has also completed a data base of emissions factors for those materials identified as potential indoor air sources.

Technical Objective: The proposed project will utilize AEERL's experience in materials life cycle and indoor environments and CERL research experience in facility design, construction and operation to expand, enhance and field test CERL's Knowledge-Based Model prototype.

Technical Approach: The technical approach will include the following components:

- Expansion of the existing model to include additional data sets (i.e., manager, owner, designer inputs);
- Development of CERL data on facilities such as the performance and costs of various systems;
- Inclusion of IAB's Indoor Air Exposure model and emissions data;
- Modification and application of AIA/IAB's Life Cycle Methodology;
- Expansion of the cataloging activity to include all construction materials;
- Interview/workshops with Experts and Users to establish knowledge base rules and data sets;
- Data gathering and analysis from primary sources; and
- Beta testing.

This project will require close coordination between the sponsoring agencies, facilities managers, designers, general contractors,manufacturers and IAQ experts.

Relationship to DoD/DOE Objectives: DoD is potentially the single largest builder and manager of facilities in the world. The proposed Knowledge-Based Model will help DoD to optimize environmental and economic considerations over the life of these facilities.

This project is directly related to DoD/DOE's Pillar 3-Pollution Prevention; Thrust 3.J.: Life cycle Environmental Assessments; item (3.III.2.d): Environmental life cycle cost model. It compliments on-going IAB research in IA emissions and control technology characterization and modified materials life cycle assessments. It also enables CERL to move from its prototype knowledge base to a full-scale, marketable decision making tool.

Relationship to Similar Work: The AIA is currently working with AEERL/IAB to compile information on the environmental impacts of selected materials which can be used by design architects. This information will be made available to the users in an electronic format.

There is no existing comparable effort to bring together such a broad array of environmental and construction data into a single expert system which will be available to such a broad range of users.

Task/Activities: Tasks for project completion:
1) Incorporation of IAQ Exposure Model;
2) Beta Test of expanded knowledge base model
3) Acquisition/development of pertinent data sets
4) Development of pre-production knowledge based model
5) Optimization and beta test of model
6) General Distribution

Technical issues to overcome involve the restructure of the prototype model to include IAQ components, expansion of the model to accommodate the CERL and IAB data sets, acquisition and development of new data, quality assurance, and optimization of final knowledge base.

8. Expected Payoff:

Potential Users: The Users include architects, engineers (e.g. HVAC engineers), facilities designers, construction managers, public agencies (e.g., GSA, Corp of Engineers, etc.), state and federal policy makers, and materials manufacturers.

Impact: The model will promote environmentally-sensitive decision making throughout a facilities life cycle. The impacts of this approach to decision making to the various components of the life cycle include the following:

Building materials' and equipment manufacture:
- Reduced negative impact on resource consumption;
- Reduced undesirable manufacturing by-products;
- Reduced exposure to hazard (e.g.,IA contaminants).

Construction:
- Reduced undesirable waste in terms of quantity and content;
- Reduced pollution generating activities;
- Reduced human exposure to hazard

Operation and Maintenance:
- Reduced operating expenses; energy, and resource consumption;
- Improved service life
- Reduced undesirable wastes
- Reduced exposure to hazards (e.g., IAQ impacted from cleaning activities)

Disposal:
- Reduced waste and enhanced opportunities for recycle.

9. Milestones:

Complete Phase I Environmental Knowledge Base Model	5/92
Initiate Phase II Pre-production Model Development	12/93
Complete Phase II Model	12/94
Complete Phase III Model Beta testing	8/95
Release to Public	9/95

10. Transition Plan:

Successful Tech Transfer involves a strong marketing entity, capable of effective implementation in practice and/or a commercial method that sells itself by virtue of its quality and utility. The integration of this product by the Corp of Engineers, DoD, and GSA into its decision matrix for new and existing facilities will act as a driver for the broader usage. In addition, the American Institute of Architects is actively seeking to assume update and distribution responsibilities for this system in FY96 as an extension of the ERG.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	TOTAL
CERL	50	150	150	0	0	350
EPA	300	295	295	295	295	1480
SERDP	0	500	400	300	0	1200
TOTAL	350	945	845	595	295	3030

* EPA Funding for FY92-FY96 are funds spent to develop AIA/EPA's LCA materials methodology and to support the transfer of this methodology via the ERG to the User community. In addition, AEERL has spent an estimated $1,050K in the development of the components necessary to this models success. These expenditures were as follows: $300K in the development of a LCA materials methodology; $375K for developing materials catalogs; $75K in the development of IA emissions data base; and $300K in the development of IAQ models.

12. Performers:

Environmental Protection Agency/Air and Energy Engineering Research Laboratory; US Army Corp of Engineers/Construction Engineering Research Laboratory

13. Principal Investigators:

James B. White
Air and Energy Engineering Research Laboratory
MD-54
Research Triangle Park, NC 27711
TEL: (919) 541-1189
FAX: (919) 541-2157

Tom Napier
US Army Corps of Engineers
Construction Engineering Research Laboratories
P.O. Box 9005
Champaign, IL 61826-9005
TEL: (217) 373-7263
FAX: (217) 373-6724

14. Keywords:

Life Cycle Assessment, Expert Advisor, Building Materials, Pollution Prevention, Construction costs

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Advanced Zinc Phosphate Metal Pre-Treatment

3. **Agency:** Army

4. **Laboratory:** TACOM (Tank Automotive Command)

5. **Proposal ID:** #659

6. **Problem Statement:**

Goal: To eliminate the use of hexavalent chromium rinses on zinc phosphate and to enhance corrosion protection and adhesion of paint film on ferrous and non-ferrous metal surfaces prior to painting or adhesive assembly.

Targeted Department: All of DoD and the private manufacturing sector dealing in painting especially automotive assemblies such as cars and trucks.

Background: Corrosion is a issue that costs the Army an estimated $3 billion dollars/year according to a study done by the national Bureau of Standards. A major portion of this bill to the Army comes in the form of corrosion of the sheet metal and structural members of all ground vehicles. Metal surface pre-treatments such as phosphate coatings play an major role in corrosion prevention. They act as cleaners to the metal and provide a passivated surface for subsequent primer adhesion and corrosion protection. Together with the primer, they offer 75-90% of the total corrosion resistance found on painted sheet metal. Improvements thru the use of advanced metal-phosphate coatings can increase this protection in absolute terms from the current 30-90 hours in a salt spray chamber to 2000 hours. This process in real world conditions equates to an extra 5-10 years of actual service life. Patents on this and related modification of this process to include Mg-phosphate polyelectrolyte have been issued. Continued effort must be pursued to keep abreast of this new and emerging technology to bring it to full commercialization to the DoD community and industry as well.

7. **Project Description:**

Technical Objectives: is to formulate a zinc phosphate metal pre-treatment using polyacrilyc acid as an additive to enhance the corrosion and adhesion properties of current pre-treatments. The result of which will be to eliminate the hexavalent rinse that is part of the current sate-of-the-art technology, without sacrificing any performance. Secondly, we want to bring the laboratory results to commercial practice by running scale up or pilot plant production in an established commercial factory.

We have a commitment from TRW Inc to pursue such an venture once funds become available.

Technical Approach: Finish the laboratory studies at Brookhaven National Labs (BNL). Transfer this technology to the shop floor at TRW.

Validate the concept under actual production on real parts as encountered by industry. Reformulate and adjust process as dictated by the scale up studies.

Tasks:

- Finish the laboratory formulations.
- Conduct scale up studies
- Move operation to TRW shop facilities
- Order parts to be pre-treated that are representative of typical automotive assemblies such as doors.
- Conduct pilot plant operations for scale up
- Reformulate zinc phosphate pre-treatment as necessary to optimize process.
- Paint the door samples at an commercial installation
- Test sample doors for performances such as corrosion adhesion and durability using standard ASTM or SAE methods.
- Validate the whole production process by writing technical user manuals and cost validation studies.
- Present a technology transfer workshop for DoD and industry
- Write a final report

Relationship to DoD/DOE Environmental Objectives: This effort is an outgrowth of pioneering work done at Brookhaven National Laboratories in Upton, New York. The reduction of hexavalent chrome rinse is of great benefit as it eliminates a known carcinogen from the work place.

Technical Risks: Low, due to the extensive work done at BNL to date. The scale up to commercialization represents the greatest risk at this time. However, BNL track record in this area should reduce such risks and result in successful commercial implementation.

8. Expected Payoff:

Potential users is all of DoD and industry production that paints ferrous and non-ferrous metals.

Economic Impact: DoD: One time cost avoidance on the Family of Medium Tactical Vehicles is 50,000 trucks x 40 cost avoidance in not using hexavalent chrome rinse is $2,000,000 savings at DoD. For industry based in an annual 10,000,000 production of cars and trucks savings per unit are smaller due to economics of scale is $10/unit the 10 MIL x $10/unit equals $100,000,000 savings annually.

9. Milestones:

Finish lab formulations	FY95
Conduct Scale up studies	FY95
Order test doors	FY94
Conduct pilot plant scale-up	FY95
Reformulate Zn phos chemistry if required	FY95
Paint completed teste doors	FY95
Test door samples	FY96
Validate process	FY96
Write final report	FY96

10. Transition Plan:

Technology will be demonstrated to industry at TRW Inc. in New Jersey on full scale production of parts ranging from large panels to automotive fasteners. We will then write a users manual for the process.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	175	150	100	425

12. Performers:

Department/Agency: TACOM
Industry: TRW Incorporated
Planned Cooperative agreements with Brookhaven National Labs, TRW, and TACOM.

13. Principal Investigators:

I. Carl Handsy, Materials Engineer
AMSTA-UDM
TACOM
Warren, MI 48397-5000
TEL: 313 574-8834 DSN 786-8834
FAX: 313 574-6501 FAX 786-6501

Brookhaven National Labs:
Dr. Larry Kuackka/Process Materials Group

14. Keywords:

Hexavalent chromium, corrosion protection, zinc phosphate pretreatment

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys

3. **Agency:** Army

4. **Laboratory:** Army Research Laboratory Materials Directorate

5. **Proposal ID:** #673

6. **Problem Statement:**

The development and implementation of (1) a non-chromate conversion coating for aluminum alloys and (2) an alternative sealing treatment to the currently used sodium dichromate in the anodizing process for use in combat and tactical vehicles, munitions, and aircraft.

Background: Chromate conversion coatings such as the currently specified Alodine treatment have been identified as a large unacceptable source of hazardous waste generation and danger to worker health and safety. Chromate conversion coatings have been utilized to promote adhesion and corrosion resistance of organic coating systems (primer-topcoat), but efforts to develop finishing systems that do not incorporate a pre-treatment have not demonstrated comparable performance. This project which is aimed at reducing production and disposal of hexavalent chromium hazardous waste received support ($50K) in FY91 under the EAMTP (Environmentally Acceptable Materials Treatment Processes - MANTECH) program but remained unfunded in FY92 and FY93 due to limited availability of funds.

Another source of unacceptable hexavalent chromium is the sodium dichromate seal used in the aluminum anodizing process. Removal and disposal of the additional hexavalent chrome from the process waste water exacerbates the cost and the potential health safety problem. The use of non-chromate sealing system will permit an anodizer to eliminate one hazardous constituent. This effort has not been funded previously.

7. **Project Description:**

Preliminary laboratory testing at ARL Watertown (previously MTL) based on salt fog and electrochemical impedance spectroscopy showed that a Sanchem Boehmite non-chromate conversion coating was promising for several aluminum alloys. The technical objective of the proposed project is to demonstrate the efficacy of non-chromate conversion coatings and sealers for aluminum alloys without compromising corrosion resistance for Army applications and environments. Limited test results of a

non-chrome sealer, nickel acetate, for anodized aluminum indicated that this seal system could provide comparable corrosion resistance to the chrome sealer.

Because of the high performance alloys used throughout Army weapons and ammunition, and the harsh environments/extremes encountered in military service, test programs to evaluate these coatings for Army-specific applications are required. successful completion of the project will contribute to the DA and DoD goal of a significant reduction in hazardous waste generation in the 1995-1997 time frame. Technical Approach:

(1) Evaluate by a comprehensive characterization of candidate non-chromate conversion coatings (industrial sources and in-house development) for aluminum alloys 2024, 5052, 5083, 5086, 6061, 7075 (with special emphasis on the 5000 series used primarily in combat and tactical vehicles) for comparison with the currently used Alodine chromate conversion coatings. Test protocol includes Auger, ESCA and IR spectroscopy analyses, salt fog, Electrochemical Impedance Spectroscopy, adhesion, stress corrosion cracking, outdoor exposure and field tests to simulate battlefield environments. This project is considered to be low risk.

(2) Several sources of supply for the non-chrome sealer will be identified and evaluated in the laboratory with respect to corrosion resistance, abrasion resistance adhesion, fatigue life, Comparable tests will be conducted in the actual production environment to demonstrate performance equivalent to chromium sealers.

8. Expected Payoff:

Potential users include MSCs, RDECs, Depots, DoD industrial base. The P.I. of the project is a member of the Aerospace Chrome Elimination Group comprised of Army, Navy, Air Force, and industry participants (Boeing, Grumman, McDonnell Douglas, Northrop, Rockwell, Lockheed, Hughes). Use of the non-chromate conversion coating and sealing system will allow government and industry facilities to eliminate one source of hazardous waste with concomitant cost savings associated with reduction of waste treatment and disposal costs. Though an exact cost benefit analysis is not yet available, the minimal implementation costs foreseen produce a high potential for significant cost savings. In 1991 the Army's cost of safe handling and disposal of hazardous waste was estimated to be $335M. The same cost was projected to be $75B throughout the industrial base.

9. Milestones:

Non-chromate conversion coating

1.	Laboratory evaluation of commercial processes and in-house developed coating	FY93
2.	Outdoor exposure tests, field tests	FY94
3.	Specification, transition to users	FY95

Non-chromate sealing system	
1. Industry survey system	FY93
2. Production Trial	FY94

10. Transition Plan:

Coordination with MSCs, RDECs, Depots through membership in corrosion Prevention Advisory Teams (CPATS) and the Aerospace Chrome Elimination (ACE) Group; Project Reliance sub-panel AM-6.2 on Paints, Coatings and Cleaning Materials; introduce specification for non-chromate conversion coating for aluminum alloys early in the acquisition cycle of weapon system and insure flow-down to contractors, sub-tier suppliers and vendors.

Once a nonchrome sealing system has been successfully demonstrated in the production environment, the technical agency will direct the contracting officer to permit the use of the qualified nonchrome sealing system on aluminum components. Transition to the nonchrome sealing system will require draining and cleaning of the current sealing tank, to remove any residual chromium, and refilling the tank with the designated nonchrome solution.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	245	300	150	695

12. Performers:

Department of the Army, Army Research Laboratory (formerly MTL) Materials Directorate, AMSRL-MA-MA, Watertown, MA. Member of the ACE Group, cooperative development agreements with DoD and industrial base. U.S. Army, ARDEC, ATTN: SMCAR-CCH-P, Picatinny Arsenal, NJ and Production Installations

13. Principal Investigators:

John H. Beatty, AM
SRL-MA-MA
Watertown, MA 02172-0001
TEL: (617) 923-5212
FAX: (617) 923-5331

Jae Sim
US Army, ARDEC
SMCAR-CCH-P
Picatinny Arsenal, NJ 07806-5000
TEL: (210) 724-6515
FAX: (210) 274-3793

14. Keywords:

Conversion coatings, aluminum alloys, hexavalent chromium reduction, Sanchem Boehmite

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** High-Performance, Lead-Free Electrical Sealants

3. **Agency:** DOE

4. **Laboratory:** Sandia National Laboratories (SNL)

5. **Proposal ID:** #429

6. Problem Statement:

High-performance, electrical-grade polysulfide (MIL-S-8516F) is used Extensively throughout the DoD as a fuel-resistant sealant for electrical components in aircraft; it is also used as a sealant by the DOE to protect warhead arming, jusing, and firing sections, which operate at medium to high voltages. However, electrical-grade polysulfide contains lead oxide, a hazardous material that will be subjected to strict Environmental Protection Agency (EPA) regulations in the near future. A lead-free material meeting the high performance DoD and DOE design requirements needs to be found. Finding such a material will help the Pollution Prevention SERDP Thrust Area achieve its objective of reducing the use of lead, one of the hazardous substances targeted by EPA. Work will also be performed to see if toluene sealant solvents, also targeted by the EPA, can be replaced with nonhazardous solvents.

This program would be a continuation of DOE/ECM-funded seed project. The beginning of the program would be applied research to develop a nonhazardous material substitute. This would be followed by technology transfer to both aerospace and DOE-integrated suppliers, contractors, and repair depots.

7. Project Description:

Understandably, it will be challenging to find a lead-free sealant that would be a completely compatible drop-in for MIL-S-8516F. This material has been in use for more than twenty years has had many of it's problems ironed out through field experience and constant tweaking. Thus, our first effort for 1994 will be to develop a viscosity envelope for evaluating the flow of both the lead-containing polysulfide and alternative materials such as lead-free polysulfides and thioethers. Understanding sealant rheology is particularly important to insure that the alternative sealants can fill narrow channels and gaps. Long-term reliability testing will also be required for the new lead-free sealants so that they can qualify for the stated high-performance applications. Stability of the formulated production material needs to be determined n order to determine shelf life, particularly for field repairs. Production lot material identification by "finger printing" should be developed to reduce supplier packaging cost and insure product reliability. We would introduce an innovative procedure for accurately tracking each lot from supplier to government application. This is based on the work of two of the project participants, Keenan and Shepodd, who have developed material tagging procedures for addressing several national security issues. Better material and process characterization information will be used in the rewriting or issuing of a new specification.

In addition to evaluating polysulfide formulations with non-lead additives, this project will investigate the feasibility of using non-polysulfide formulations. For example, extensive work done by Courtaulds, Inc. indicates that polythioether may be a viable candidate as replacement for the standard polysulfides. The cure rate for this material is easier to control than that of polysulfides because moisture is not part of the curing process. Also, available to other sealant manufacturers.

Finally, we plan to investigate encapsulants that do not rely on toluene solvents. Work performed to date indicates that polythioether may not require toluene solvents.

The major technical challenge is this project is identification of suitable lead-free formulations that can be developed into electrical-grade sealants capable of meeting the stringent requirements of MIL-S-8516F. These formulations will be identified as early as possible in the project (before the end of the first year--see milestone 2 in Section 9) to determine whether further product testing and development, material fingerprinting development, specification development, and commercial source development should proceed.

8. Expected Payoff:

There is a strong likelihood that lead-containing (8516 type) polysulfides will be difficult or nearly impossible to acquire within the next few years because of stricter requirements placed on hazardous waste minimization. Also, vendors are finding it difficult to obtain the proper grade of the required lead peroxide curative. Another issue is the supplier may have to assume cradle-to-grave responsibility (currently under discussion at EPA) for these materials. This project will cooperate with the interested government agencies and vendors in order to develop an environmentally friendly, drop-in material that can provide solutions to these concerns.

9. Milestones:

1.	Viscosity evaluation incorporated to sealant performance specification	5 mo
2.	Lead-free materials identified for testing*	11 mo
3.	Material compatibility testing	17 mo
4.	Material fingerprinting procedure specified as new method to tag vendor production lots	22 mo
5.	Rewrite MIL-S-8516 (a new specification may be issued)	26 mo
6.	Develop a other commercial sources	31 mo
7.	Investigate solvent-free material system	34 mo

* If suitable candidate lead-free sealants cannot be identified, project will end at this date.

10. Transition Plan:

Instead of having government laboratories develop a new material by themselves, we would work with up to four potential vendors to formulate a new material. The DoD and DOE facilities would provide specification requirements, extensive testing, general guidance for formulation, and methods for material control that will lower their production cost. Because of the high performance nature required of these materials, only small-scale private sector, technical dual-use potential is anticipated. When a solvent-free material (late in the program) is developed, applications for a CRADA would assist in the transfer in the use of new generations

of sealants to application like sealing and encapsulating concentrator solar assemblies instead of using silicones. This could realize a large material cost savings.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	110	280	300	230	920
DoD	10	50	50	50	30	190
DOE	530	200	250	250	200	1430
Total	540	360	580	600	460	2540

12. Performers:

DOE performer is Sandia National Laboratories. DoD performers are the Navy Air Warfare Center in Warminster and the Materials Directorate at Wright Patterson Air Force Base. Also the General Services Administration - Federal Supply, in Auburn, WA.

13. Principal Investigator:

Dr. John A. Emerson
Sandia National Laboratories
Organic Materials Department, 2472
Albuquerque, NM 87185-0979
Phone: (505) 845-9747
FAX: (505) 844-1110
E-mail: jaemers@sandia.gov

14. Keywords:

Hazardous waste generation, Polysulfide, Polythioether, Lead, MIL-S-8516, Sealant, Fuel resistance, Potting material, Connectors

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Reduce VOCs and HAPs from Painting and Cleaning Operations

3. **Agency:** Environmental Protection Agency

4. **Laboratory:** Air and Energy Engineering Research Laboratory

5. **Proposal ID:** #316

6. **Problem Statement:**

Goal: The goal of all US Marine Corp Commodity Centers (MCCC) and Department of Defense facilities is to comply with all Federal, State and Local pollution regulations through the use of Pollution Prevention (P2) or end of pipe technologies. Painting and surface cleaning processes conducted at DoD facilities reportedly represent a significant portion of the Hazardous Air Pollutant (HAP) and Volatile Organic Compound (VOC) discharges to the atmosphere. The total discharge to the environment each year from DoD and related commercial operations is reported to be over 100,000 tons. Thus, DoD facilities must be prepared to demonstrate and apply techniques which prevent or eliminate VOC and HAP discharge to the atmosphere. This proposal is a continuation of the program to develop and evaluate P2 and abatement options that eliminate the use or discharge of HAPs and VOCs to the atmosphere. The program will continue to identify, develop, and evaluate substitutes for hazardous solvents such as methylene chloride, methyl ethyl ketone, and 1,1,1 trichloroethlyene which can typically be found in DoD maintenance operations.

Background: In the FY93 SERDP authorizations, this program was approved to develop and evaluate process P2 and spray booth emissions reduction techniques. The program was initiated in late 1993 with a P2 survey of manufacturing processes used at MCCC at Albany, GA and characterization of paint spray booths at the MCCC at Barstow, CA. Processes at these facilities typify most USMC and DoD depot logistics maintenance center operations. The initial P2 surveys identified a number of processes that may be amenable to innovative P2 techniques when properly engineered and incorporated into the operation. The processes observed are common to most maintenance and metal processing facilities; thus, results of the program would be immediately transferrable to other similar DoD and commercial facilities. They included surface cleaning such as degreasing and wipe cleaning, high- efficiency painting processes utilizing undiluted high-solids paints, high-efficiency painting equipment, and the elimination and substitution of process operations which discharge hazardous compounds to the atmosphere. Preliminary laboratory evaluations of the proposed alternatives are presently being conducted to evaluate the compatibility of the options with the process materials.

The program also initiated a technology development and demonstration activity to validate the recirculation/partitioning concept used with a novel ultraviolet light/ozone, UV/ozone, oxidation technique to eliminate HAP and VOC discharges from paint spray booths. The preliminary results of these studies suggest that booth discharge flow reductions of up to 75% can be achieved. This reduction of discharge volume from the process will result in a corresponding reduction of pollution control capital and operating costs as well as an increase of control system efficiency.

7. Project Description:

Technical Objective: Many low polluting techniques can be transferred from other industries where they have proven successful. These techniques can range from simple process modification or elimination, or changes in the process schedule or to the use of substitute materials. Many of the techniques identified have been used by industries outside the metal finishing and fabrication category and thus need only to be demonstrated for DoD applications. The request will continue the program initiated in FY93 to evaluate and present results in appropriate DoD and commercial technical and manufacturing literature. Each option will require study and evaluation to assess the consequences of the process change on operations and materials. Based on the preliminary facility survey, CO2-based cleaning technologies may be applicable to a broad range of depot cleaning requirements and require only the development of appropriate process fixtures and processing procedures.

The Phase 1 studies also concentrated on paint spray booths. This project will extend the results of the FY93 recirculation/partitioning, UV/ozone research and development program to a broader range of booth designs and expanded UV/ozone technology capability.

Technical approach: This phase of the program will continue laboratory evaluations of the UV/ozone technology and of pollution prevention concepts to eliminate the discharge of paint solvents to the atmosphere. These studies will quantify the efficiency and technical feasibility of the selected P2 concepts to: serve as a substitute for the polluting process material or evaluate the results of a process modification to reduce the discharge of the process pollutants to the atmosphere. This phase of the program will be accomplished by field evaluations at selected United States Marine Corps (USMC) maintenance facilities. The program will also continue fundamental research studies, initiated in FY93, of the UV/ozone oxidation technology for destruction of VOC and HAP compounds. It will expand the recirculation/partitioning concept to include all booth designs including down draft and side draft spray booths.

Based on the preliminary studies completed during Phase I of this program, which identified sources and opportunities for P2 studies, detailed technical and economic evaluations will be conducted on each selected process and P2 technique. The US Marine Corps logistic centers at Albany, GA and at Barstow, CA will serve as beta test sites for the P2 options selected for evaluation during the program. Sources identified at the Albany, GA facility during the initial survey include degreasing, painting, painting equipment cleaning, small parts cleaning, and general surface cleaning. Each of these processes use and discharge organic solvents to the atmosphere. Alternative P2 techniques selected as demonstration candidates include CO2 based cleaning technology, process elimination, substitution of aqueous and semi-aqueous cleaning agents, and equipment changes which will achieve greater processing efficiency. Extended field testing and evaluations of the proposed options are scheduled to commence in early 1994. Surface cleanliness, ease of operation, cost of installation and operation, and resulting process efficiency will be determined during the evaluations. The results of these evaluations will provide the technical background for the development of process manuals to implement technology transition to DoD and the commercial industry.

Laboratory research and development activity will continue to upgrade the UV/ozone technology. The Phase 1 program completed installation of the laboratory pilot system to conduct extensive studies of the concept and to develop a fundamental understanding of the UV/ozone pollutant destruction technology. Data will be collected from an operating field unit and transferred in real time to the laboratory pilot system. The field conditions will be simulated

and evaluated in the pilot unit under laboratory conditions. The results of the laboratory studies will be transferred back to a field unit to facilitate improvements and upgrading of the operating efficiency of the system.

8. Expected Payoff:

Successful completion of this program will allow most DoD facilities to define pollution control strategies using proven P2 techniques. A 60 to 95 percent reduction in VOC and solvent discharges from the respective processes can be expected.

The immediate benefits of the program will be at MCCC Barstow, CA. The program will provide the facility and other DoD facilities with P2 options which can significantly reduce the cost of emissions reduction while greatly reducing the discharge of hazardous pollutants to the atmosphere. The resulting technology transfer of P2 technology options developed or evaluated during this program will also assist private businesses in reducing their negative impact on the environment and reduce the adverse economic burden imposed by costly control devices.

There have been no technical problems during Phase 1 to prevent successful completion of the program. Preliminary emission characterization studies have confirmed the predicted pollutant concentration levels expected in the test spray booths. Based on these predictions, a minimum 60 to 70 percent reduction of emissions flow volume will be achieved. This reduction will result in a corresponding reduction of emissions control capital and operating costs for the selected operations and P2 options.

9. Milestones:

Completed P2 facility survey and recirculation baseline studies.	3 mo
Identification, selection, and design of P2 Mods.	6 mo
Installation of P2 and booth recirculation mods.	9 mo
Testing and evaluation of P2 options	12 mo
Preparation of final reports and process design manuals series	20 mo

10. Transition Plan:

Work accomplished during this program is intended to provide information on the performance and cost of innovative pollution reduction approaches for VOC and air toxic emissions. These techniques will be reported in applicable manuals and journals. The test results will be presented in a series of design and process implementation manuals that present the capabilities, limitations and efficiency of the options studied. The manuals will be suitable for development of similar pollution abatement strategies at other facilities. Technology transfer and assistance programs such as the EPA's Control Technology Center (CTC), Pollution Prevention Information Clearinghouse (PPIC) and similar DoD programs will be used to transition the technical results into the DoD and commercial community. Contact with the EPA's CTC has been established to present the results of the studies to its clients.

11. Funding: ($K)

	FY93	FY94	TOTAL
SERDP	2750	600	3350
USMC	1000	0	1000
TOTAL	3750	600	4350

12. Performers:

The US Marine Corps, Marine Corps Logistics Bases (MARCORLOGBASES) Albany, GA maintains program oversight. The USMC is responsible for maintaining liaison and coordination between the program participants and the US Marine Corps bases where the demonstrations are taking place.

The Advanced Research Laboratory, Penn State University, State College, PA is conducting research on the UV/ozone technology.

The Research Triangle Institute, Research Triangle Park, NC will conduct the P2 studies of alternatives which can be incorporated into maintenance operations at the various bases.

The EPA's Air and Energy Engineering Research Laboratory at Research Triangle Park, NC has primary management responsibility for the program. AEERL is responsible for overall coordination of research and development activities at the participating facilities. It will conduct all emissions testing to evaluate the capability and efficiency of the options tested.

13. Principal Investigator:

Charles H. Darvin
US Environmental Protection Agency, MD-61
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711
Tel: (919) 541-7633
Fax: (919) 541-2157

14. Keywords:

Solvents, Painting, Spraybooths, Cleaning, Spray Gun, VOC

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Aircraft Maintenance Chromium Replacement

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division, Warminster

5. **Proposal ID:** #066

6. **Problem Statement:**

To replace chromates (Cr) currently used in aerospace materials and processes on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Chromium VI is a carcinogen. Federal, state and local environmental agencies (EPA, California's Air Quality Management Districts (AQMD), etc.) are restricting the use and disposal of this hazardous material through regulations such as the Clean Air and Water Acts, CERCLA, and RCRA along with local EPA and AQMD rules. In addition, OPNAV and CNO directives require significant reductions in the amount of hazardous waste generator by the Navy. Chromated materials used in production and depot level maintenance operations are a large contributor to this overall waste generation. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, chrome-free alternatives have to be developed. This work is covered under the Tri-Service EQ Strategic Plan Pillar 3: Pollution Prevention: Requirement Thrust: 3.A.3: Metal Working/Processes Plating/Finishing and is a continuation of an existing SERDP 6.2/6.3 environmental effort.

7. **Project Description:**

Non-chromate alternative materials and processes will be investigated for current anodizing, pretreating, sealing, adhesive and corrosion preventive processes. The approach taken for the development of non-chromate materials will be identification, development, test & evaluation, demonstration and implementation. Chromic acid anodizing (CAA) is a common inorganic coating for pretreating aluminum prior to painting. As an example, this program identified the best alternatives to CAA from existing and developmental coating methods. These alternatives included thin sulfuric, phosphoric acid anodizing and Boeing Aerospace Corp's Sulfuric-Boric Acid Anodize (SBAA). Selected alloys were processed and tested to determine which replacement systems provided equivalent corrosion resistance and paint adhesion while maintaining the existing mechanical properties provided by CAA. After lab optimization, a SBAA production process was demonstrated at the Naval Aviation Depot (NADEP) at North Island. After successful completion of the service demonstration, the MIL-A-8625 Anodize specification was modified and the process is being transitioned to full fleet implementation. This approach will be taken for the development of non-chromate pretreating materials (alkaline cleaners & deoxidizers, etc.), adhesives, sealants, and other aerospace chrome containing corrosion preventive materials.

8. Expected Payoff:

The elimination of chromic acid anodizing, chromated alkaline cleaners & deoxidizers, and sealants & adhesives, significantly reduces the total amount of chromium emitted from Navy operations. Elimination of chromic acid anodizing also eliminates the need for expensive emission control equipment (estimated at $1M per Depot facility) required by CAA and AQMD legislation. Non-chromated alkaline cleaners and deoxidizers, developed under a Pollution Abatement funded program have been implemented at three NADEPs to meet these new regulations. NADEP Jacksonville has reported an annual cost savings of $23K and a reduction of 3 tons of chromium waste per year from the use of the non-chromate deoxidizer. Furthermore, these alternatives significantly reduce rising disposal costs of chromium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transition to commercial airlines, automotive industries, equipment manufacturers, etc.

9. Milestones:

1.	Identify Major Cr Sources/Initiate Development Efforts	09/90
2.	Develop/optimize non-Cr cleaners & deoxidizers	07/91
3.	Initiate Non-Cr acid anodize alternative development	09/91
4.	Transition/implement non-Cr cleaners & deoxidizers	06/92
5.	Evaluate/optimize Non-Cr acid anodize processes	12/92
6.	Initiate non-Cr adhesive pretreatment development	12/92
7.	Service demonstration & anodize spec revision (non-Cr)	08/93
8.	Evaluate non-Cr adhesive pretreatments	12/93
9.	Initiate non-Cr adhesive bond primer development	12/93
10.	Implementation of non-Cr anodize	03/94
11.	Optimize non-Cr adhesive pretreatments	09/94
12.	Evaluate non-Cr adhesive bond primers	09/94
13.	Service demonstration of non-Cr adhesive pretreatments	06/95
14.	Advanced development of non-Cr conversion coatings	06/95
15.	Optimize non-Cr adhesive bond primers	09/95
16.	Optimize water-borne non-Cr adhesives	09/95
17.	Initiate non-Cr pretreatment strippers development	11/95
18.	Service demonstration of non-Cr conversion coatings	05/96
19.	Transition of non-Cr adhesive pretreatments	08/96
20.	Service demonstration of non-Cr adhesive bond primers	09/96
21.	Initiate water displacing corrosion preventatives	10/96
22.	Transition of non-Cr adhesive bond primer	06/97
23.	Transition of water-borne non-Cr adhesives	06/97
24.	Evaluate water displacing corrosion preventatives	09/97
25.	Initiate water-borne non-Cr adhesives evaluation	09/97
26.	Service demo water displacing corrosion preventatives	06/98
27.	Service demonstration water-borne non-Cr adhesives	09/98
28.	Transition of water displacing corrosion preventatives	09/99
29.	Transition water-borne non-Cr adhesives	09/99

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials will insure availability for implementation. For example, non-chromated alkaline cleaners and deoxidizers have been fully implemented at three NADEPs to meet these new environmental regulations. The SBAA process has been successfully demonstrated at NADEP North Island and is currently being transitioned to fleet use.

11. Funding: ($K)

FY	90	91	92	93	94	95	96	97	98	99
Navy	110	110	150	250	--	--	--	--	--	--
SERDP	--	100	88	170	180	350	350	300	310	230
TOTAL	110	110	298	290	350	350	350	300	310	230

12. Performers:

Evaluation/demonstration of Chromium-free alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. This effort is being coordinated with the Army Research Laboratory (Watertown, MA), the Air Force (Tinker ALC and Tyndall AF Civil Engineering Services Center), National Defense Center for Environmental Excellence (Non-Chromate conversion coating demo) and aerospace industries (Boeing, Rohr, Grumann, MDA-E, Lockheed, etc.).

13. Principal Investigator:

Stephen J. Spadafora
Naval Air Warfare Center Aircraft Division Warminster
P.O. Box 5156 (Code 6062E)
Warminster, PA 18974-0591
Phone: (215) 441-2704
FAX: (215) 441-1925

14. Keywords:

Chromium Elimination, Pretreatments, Materials Substitution, Surface Preparation, Anodizing, Adhesive bonding

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Dry Nitrogen for Ship Boiler Layup

3. **Agency:** Navy

4. **Laboratory:** Naval Facilities Engineer Service Center (NFESC)

5. **Proposal ID:** #055

6. **Problem Statement:**

The overall goal of this project is to eliminate the use of hazardous solutions for lay-up of naval ship's boilers. At the present time, ship's boilers are laid-up using an aqueous solution of sodium nitrite to prevent oxidation of the interior of the boiler tubes. Disposal of waste sodium nitrite solution produced when a boiler is taken out of lay-up is a significant hazardous waste disposal problem. The nitrite solution must be either chemically treated to reduce the nitrogen to the form of nitrogen gas or hauled away by a hazardous waste disposal contractor. Both of these options are very costly. This project proposed to demonstrate the use of dry nitrogen gas in lieu of sodium nitrite for lay-up of boilers. This project supports the SERDP pollution prevention goal of reducing hazardous waste generation through process changes to key industrial operations. The SERDP research and development objective is to eliminate hazardous waste generation from corrosion protective processes. The requirement for this research is unique to the Navy. This is a new project in technology demonstration (6.3).

7. **Project Description:**

The technical objective of this project is to determine the technical and economic feasibility of using dry nitrogen gas to lay-up ship's boilers. In recent years, improved membrane and pressure swing adsorption systems have become commercially available. These improved systems have greatly reduced the cost of producing clean, dry nitrogen gas while improving reliability and maintainability. This project will assess the technical, operational, and economic feasibility of using dry nitrogen gas as a replacement for sodium nitrite solution for boiler lay-up. A review of commercially available nitrogen separation processes will be conducted. Concurrently, a review will be made of ship operational requirements and constraints. Reliability, operability, maintenance, training, and other logistics issues will be reviewed and assessed. A prototype dry nitrogen lay-up system will be designed in sufficient detail to permit generation of accurate capital and operating cost figures. Technical and economic feasibility will be documented in a phase 1 final report. If phase 1 indicates that dry nitrogen boiler lay-up is technically and economically attractive, a program of field demonstrations of this technology will be proposed as phase 2. This project is assessed to be a low technical risk project: all of the hardware required to demonstrate this technology is believed to be commercially available. Economic, operational, and logistic issues are believed to be the major constraints. This project addresses requirement thrust 3.E (Other Hazardous Wastes) of the Tri-Service Environmental R&D Strategic Plan.

8. Expected Payoff:

The expected benefit of successful demonstration of dry nitrogen gas for boiler lay-up is the elimination of a significant source of liquid hazardous waste. The estimated cost of disposal of sodium nitrite solution by the Navy was $ 20 M in 1992. A possible additional advantage to using nitrogen gas for lay-up is a reduction in the time required to purge the boiler and get underway. This project has high transition potential because dry boiler lay-up could probably be implemented at any port were ship boilers are presently laid-up.

9. Milestones:

1. Phase 1: Review of N_2 separation processes including purity, cost, reliability maintainability, and capacity data completed	03/95
2. Review of ship operational requirements, lay-up requirement & specification, operational constraints complete	04/95
3. Analysis of N_2 supply system support requirements such as personnel and training	
4. Engineering design and cost benefit analysis completed	07/95
5. Final report including recommendations for demonstration project completed	
6. Phase 2: Technology demonstration plans prepared	01/96
7. Hardware for demonstration procured	08/96
8. Field demonstrations completed	03/97
9. Technology transition package completed	10/97

10. Transition Plan:

If the results of Phase 1 of this project indicate that dry nitrogen lay-up of ship's boilers is technically, operationally, and economically feasible, a proposal for field demonstration will be prepared. Following successful field demonstration (Phase 2), a technology implementation package consisting of specifications, plans, and a user data package will be prepared.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	185	490	265	940

12. Performers:

Naval Facilities Engineering Service Center.

13. Principal Investigator:

Mr. Richard Kirts P.E.
Naval Facilities Engineering Service Center
560 Center Drive
Port Hueneme, CA
Phone: (805) 982-1334 FAX: (805) 982-1409

14. Keywords:

Boiler Lay-up, Sodium Nitrite, Ship wastewaters

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Solvent Substitution and Low VOC Cleaners

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Warminster

5. **Proposal ID:** #067

6. **Problem Statement:**

To identify low VOC (volatile organic compound) content cleaning solvents for use on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE) and to identify replacements for methylene chloride based chemical paint strippers. Volatile organic solvents such as methyl ethyl ketone (MEK) are used for solvent wipedown of aircraft prior to painting and post-painting cleanup. Other procedures require the use of stoddard solvent for cleaning aircraft parts in solvent tanks. Other degreasing and cleaning methods use high VOC cleaners. In addition, current chemical paint strippers containing hazardous components like phenols, methylene chloride and chromates and paint removal operations at maintenance depots have been determined to be a major contributor to hazardous waste generation in the DoD. Recently, OSHA has reduced the permissible exposure limit for methylene chloride from 400 ppm to 50 ppm, forcing users to make extensive changes in ventilation and personal protection. Regulations like the Clean Air and Water Acts, CERCLA, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, OPNAV and CNO directives require significant reductions in hazardous waste. Therefore, low VOC non-toxic alternatives to solvent cleaners need to be developed. In addition, there is a need to evaluate alternative chemistries for paint removers for use at Naval Aviation Depots in order to identify a product or a chemistry capable of satisfying existing and future regulations while maintaining aircraft performance and operational readiness. This effort is covered under the Tri-Service EQ Strategic Plan: Pillar 3: Pollution Prevention, Requirement Areas: 3.A.3: Metal Working/Cleaning and Degreasing and 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

7. **Project Description:**

Solvent cleaners must be effective on a diverse combination of soils from baked on carbon to aircraft greases and lubricants. This program will develop solvent blend formulations and aqueous cleaners which will be evaluated with laboratory performance and cleaning efficiency tests. The best materials will be further evaluated for vapor pressure, odor, evaporation rate, safety and cost. Enzyme cleaners, lubricant cleaners, low VOC solvent cleaners, and supercritical CO_2 cleaning methods will also be evaluated in this program. Optimized materials will be service tested at a NADEP and transitioned to fleet use through specification modification and design changes. Non-methylene chloride alternatives must exhibit workable performance characteristics while reducing the impact of stripper waste on disposal operations. Because there are so many different substrates/alloys and coating systems currently used by the Navy, non-hazardous paint removers will also have to be versatile. This program will identify the best alternatives for ambient coating removal operations. Procedure efficiency, effects on substrate

surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. The best alternative material will be demonstrated at a NADEP and transitioned to fleet use through specification modification and design changes.

8. Expected Payoffs:

The development of low VOC solvents would significantly reduce the total amount of hazardous material emissions generated. In addition, the elimination of the methylene chloride based chemical paint strippers would significantly reduce the total amount of hazardous materials generated by Navy maintenance facilities and eliminate the need for expensive emission control equipment ($1M/Facility). This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and waste disposal costs, Navy aircraft and equipment must be properly maintained. This is particularly important considering the cost of A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial aerospace, automotive, and marine industries.

9. Milestones:

1.	Develop biodegradable turbine engine cleaner	09/91
2.	Optimize biodegradable turbine engine cleaners	06/92
3.	Evaluate alternative stripper chemistries (Joint Navy/Air Force Program)	09/92
4.	Service demo of biodegradable turbine engine cleaners	06/93
5.	Initiate low VOC wheel well cleaner evaluation	09/93
6.	Evaluate/optimize stripper process parameters (Joint Navy/AF Program)	09/93
7.	Initiate no VOC A/C exterior cleaner evaluation	01/94
8.	Transition biodegradable turbine engine cleaners	03/94
9.	Develop low VOC wheel well cleaners	06/94
10.	Service demonstration of optimized stripper materials (Jt. Navy/AF Program)	09/94
11.	Initiate enzyme cleaner evaluation	03/95
12.	Develop no VOC A/C exterior cleaners	06/95
13.	Service demonstration of low VOC wheel well cleaners	09/95
14.	Implementation of optimized non-hazardous strippers (Joint Navy/ Air Force Program)	12/95
15.	Evaluate/optimize enzyme cleaners	06/96
16.	Service demonstration of no VOC A/C exterior cleaners	06/96
17.	Implement optimized low VOC wheel well cleaners	09/96
18.	Initiate supercritical CO_2 cleaning investigation	09/96
19.	Investigate lubricant low VOC solvent cleaners	12/96
20.	Service demonstration of optimized enzyme cleaners	06/97
21.	Implement no VOC A/C exterior cleaners	09/97
22.	Evaluate/Optimize supercritical CO_2 cleaning methods	09/97
23.	Evaluate/Optimize lubricant low VOC solvent cleaners	09/97
24.	Implement optimized enzyme cleaners	06/98
25.	Service demonstration of supercritical CO_2 cleaning	09/98
26.	Service demo of lubricant low VOC solvent cleaners	12/98
27.	Implement supercritical CO_2 cleaning	09/99
28.	Implement Lubricant low VOC solvent cleaners	09/99

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through the Lead Maintenance Technology Center for Environment. These materials will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

11. Funding: ($K)

FY	91	92	93	94	95	96	97	98	99	TOTAL
Navy	--	--	58	--	--	--	--	--	--	58
DERA	30									30
SERDP	149	151	170	150	220	350	300	310	230	2030
TOTAL	179	151	228	150	220	350	300	310	230	2118

12. Performers:

Development of non-methylene chloride paint strippers is being performed by the Naval Air Warfare Center Aircraft Division Warminster (NAWCADWAR) and the Air Force (Tyndall AFB) in a joint effort. The solvent substitution and low VOC cleaner efforts are being performed by NAWCADWAR, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment and are being coordinated with efforts by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), DOE and aerospace industry (MDA-E, Boeing, etc.).

13. Principal Investigator:

Stephen J. Spadafora
Naval Air Warfare Center
Aircraft Division Warminster
P.O. Box 5156 (Code 6062E)
Warminster, PA 18974-0591
TEL: (215) 441-2704
FAX: (215) 441-1925

14. Keywords:

Solvents, Chemical Paint Strippers, Materials Substitution, Cleaners, Volatile Organic Compounds, Methylene Chloride Replacement

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Chemical Surface Preparation

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center

5. **Proposal ID:** #130

6. **Problem Statement:**

Conventional cleaning and surface treatment processes used in the aerospace industry often involve use of toxic materials and solvents and generation of aqueous hazardous waste streams. These processes involve toxic hazards in the workplace, risk of uncontrolled releases of hazardous substances, and treatment and disposal procedures which are costly, administratively burdensome, and attended by serious legal and financial liabilities. In addition, many traditional materials, such as ozone depleting chemicals, are subject to bans on production and use.

The development of advanced metal surface preparations that do not require use or generation of hazardous substances is needed.

This is a FY93 Funded SERDP project, requiring FY94 Continuation.

7. **Project Description:**

Technical Objective: The objective is to identify, develop, and optimize non-wet chemistry approaches for the formation of stable morphologies on the surface of aluminum, titanium and copper materials that will allow performance of high quality coating or adhesive bonding.

Technical Approach: This program will involve laboratory R&D, process scale-up, specifications development, and technology transition in two specific technical areas. These areas are (1) laser surface preparation of aluminum and titanium alloys. The feasibility of the use of the eximer laser to grow oxides on aluminum has been shown, and the bondability to both coatings and adhesives has been demonstrated. (2) non-chemical surface morphologies for coating and bonding to aluminum, titanium, and copper can be achieved via non-chemistry based processes including plasma spray, flame spray, and vapor deposition. These approaches are based on new technology and initial feasibility has been demonstrated. Processes currently in use are based on wet chemistry and require use of soluble chromate, strong acids and bases and large amounts of water. The use and generation of toxics is an increasingly risky and expensive proposition. The new approaches represent a radical, but environmentally benign, departure from existing technology. There are no serious technological roadblocks foreseen in the scale-up of these processes.

Previous efforts/accomplishments in this area within and outside the organization: This technical effort will build on recent efforts in cooperation with EOARD to develop CO_2 laser surface modification technology.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. In some instances, elimination of ozone depleting chemicals (ODCs) may be achieved. This project will support the Air Force goal to reduce hazardous waste generation by 50% by the end of 1999 (1992 baseline).

Related activities include work on solid state cleaning of metals and thin film deposition technology, the AF Civil Engineering Support Activity (AFCESA) spray casting program and thin film (including sol gel) deposition technology developed for the electronic and commercial construction industry.

Tasks/activities: Experiments will be conducted to determine the feasibility of developing surface oxide morphologies that are thermodynamically stable, mechanically strong, and resistant to corrosion (chemically stable).

Technology areas to be investigated will include sol gel films, thin film deposition of SiC, SiN, SiO, sputtered and enhanced ion-beam deposition coatings as well as laser enhanced oxide formation.

- Surface laser characterization will be accomplished using various surface analysis techniques.
- Chemical and thermodynamic stability of coatings will be determined.
- Corrosion resistance and performance of coatings and adhesive bonded joints will be studied.
- Bench top process equipment will be developed and process parameters optimized.
- Testing and analysis will continue and life cycle cost studies will be performed.
- Scale up to pilot size equipment will be accomplished.
- Specifications and standards will be written.
- Processes will be optimized.
- Pilot scale equipment will be operated so that users may have short production runs performed on components prior to more extensive field\service applications.

Technical issues to overcome: The technical risks include the ability to produce the desired oxide morphology with the requisite thermodynamic and chemical stability and the needed mechanical strength without degrading the substrate mechanical properties. Attending these risks are the challenges of developing technology that will be environmentally acceptable and affordable.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.B.1
Requirements Category:	I.4
Work effort:	Tech Base

8. Expected Payoff:

Breakthrough technologies to prepare metal surfaces in various stages of manufacturing and remanufacturing will be of enormous benefit to aerospace and other industries in the US and worldwide. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, they may be offset by eliminating the costs of hazardous materials and waste management and environmental compliance and response.

9. Milestones:

1.	Project go-ahead	10/93
2.	Initiate laboratory development and tests of candidate materials and processes. Define processes to be replaced and applicable specifications and standards. Define process mechanisms and critical process parameters.	11/93
3.	Select candidate processes for more extensive testing.	12/94
4.	Select most promising materials and processes for more extensive testing.	03/95
5.	Initiate large laboratory scale process studies. Initiate process parameter sensitivity studies.	06/95
6.	Initiate studies on surface stability and strength. Initiate coating and bonding studies.	09/95
7.	Complete all preliminary tests and studies. Initiate scale-up to pilot scale process facility.	12/95
8.	Initiate optimization of pilot scale process. Begin treatment of customer furnished components for extended service evaluation. Prepare or revise specifications and standards.	02/96

10. Transition Plan:

The proposed R&D program will be accomplished in an integrated program development mode. The pilot plant will be operated at the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB, OH or at one of the Air Logistics Centers in cooperation with a user team. Successful service experience along with specifications and standards will enable each prospective user to implement processes meeting their specific needs. Potential users will be an integral part of the R&D team to ensure that their inputs will be incorporated on a continuous basis into the technology development cycle.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	300	998	1165	2463

12. Performers:

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate (WL\ML), Wright-Patterson AFB, OH 45433.

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans demonstration to be conducted either at an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio.

13. Principal Investigator:

T. J. Reinhart
WL/MLSE
2179 12th Street, Suite 1
Wright-Patterson AFB, OH 45433-6703
TEL: (513) 255-3691
FAX: (513) 476-4419

14. Keywords:

Coating, Bonding, VOCs, Hazardous Air Pollutants, Corrosion Protection, Ozone depleting substances

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Solid State Metal Cleaning

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center

5. **Proposal ID:** #116

6. **Problem Statement:**

The goal of this project is to develop innovative metal cleaning processes that do not require the use of water or volatile organic compounds (VOCs).

Cleaning of metals is a mandatory step in the processing of aircraft components, including wing skins, fuselage panels and bulkheads, etc., prior to surface preparation, such as anodizing, and subsequent priming in preparation for coating or adhesive bonding. State-of-the-art cleaning processes now involve the use of PD 680 type solvents, chlorinated solvents, or water based cleaning systems to remove oil, waxes and particulates from the surface of component surfaces.

This is a FY93 Funded SERDP project, requiring FY94 Continuation.

7. **Project Description:**

There are two technical objectives to be achieved by this project:

(1) To develop and transition to a using customer a cleaning process for large (and small) aircraft components that do not require the use of water or VOCs.

(2) To develop a process that will allow components to proceed directly to the next step in the process for surface without the need for subsequent treatments involving water or organic solvents.

Research and development (R&D) will be performed to study the mechanisms and kinetics of solid state soil (oils, waxes, particulates and metallic oxides) removal processes. Various processes will be studied including activated particulates or polymers, carbon, starch, CO_2 and various inorganic particulates including carbonates and phosphates. Studies will include assessment of how clean components really need to be before they proceed to the next step in their particular processing track. Components proceeding to inspection or other intermediate process steps do not have to meet the cleanliness standards required for surface preparations such as alodine and anodize or those going into a plating or metal deposition process. Laboratory testing will be accomplished to define and measure surface cleanliness levels needed for various subsequent processing steps in order to maintain/improve the performance of subsequent operations.

Feasibility studies have been performed using activated carbon/starch/CO_2/air and other cleaning media for the removal of various types of soil and particulates. Preliminary research

has established the feasibility of this approach for the removal of a number of oily, waxy and particulate contaminants.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. The project will assist in meeting Air Force pollution prevention objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

No government sponsored work is presently ongoing/planned in this technology area.

The project encompasses these major tasks:

- Experiments to define/delineate mechanisms/kinetics of solid state soil particulates and oxides removal as a function of cleaning media, energy levels, temperatures and times, etc.
- Process studies to select/optimize cleaning process parameters and influence on substrates, mechanics, and physical properties.
- Studies to define, measure and validate cleanliness levels required for components proceeding to the next stop of their process track.
- Testing and analysis to validate that processing changes do not degrade components performance. Factors such as corrosion resistance, coating adhesion/ performance, adhesive bond durability/strength and metal plating adhesion/performance will be comprehensively studied.
- Scale-up to pilot size process to determine scalability of processing parameters previously established.
- Demonstrate/validate process on customer-designated components. Establish and approve process specifications and standards. Perform life cycle cost analysis on process.
- Transition prototype to user/customer for extended production evaluation.

Technical Issues to Overcome:

- Removal of soils/contaminants from simple/complex geometry components without using liquid.
- Ability of solid cleaners to provide wide spectrum cleaning capability under conditions not detrimental to substrate.
- Develop a safe, environmentally sound and affordable/economical process.
- Obtain adequate cleanliness levels in order to eliminate the need for follow-on cleaning operations.

Tie to Tri-service Environmental Quality R&D Strategic Plan:
Pillar Thrust Area: 3.A.2.a
Requirements Category: I.2.b and I.2.g
Work effort: Tech Base

8. Expected Payoff:

If successful, the scope of this effort will cover the gamut of industrial cleaning operations used throughout the industrialized world. Water waste streams and VOC emissions will be eliminated from industrial cleaning operations.

The goal will be to do at least the same (if not better) cleaning job than is now being accomplished using liquids, at a cost equal to or less than today's cost (with no waste streams).

9. Milestones:

1.	Project initiation/start date. Initiate experiments to select cleaning media and define process mechanisms, and critical process parameters.	07/93
2.	Complete media testing and process parameters definitions.	05/94
3.	Initiate process parameters optimization and substrate sensitivity testing. Initiate experiments to define, measure and validate surface cleanliness levels required.	06/94
4.	Complete process sensitivity studies and substrate sensitivity testing Initiate coating, bonding plating performance validation studies.	09/94
5.	Complete process optimization and initiate scale-up and assemble pilot size process.	11/94
6.	Optimize and demonstrate pilot scale operation in cooperation with user/customers.	04/95
7.	Complete all performance testing. Write up draft specifications and standards Transfer prototype to user/customer for extended production operation.	08/95

10. Transition Plan:

This research and development (R&D) program will be conducted in concert with the Air Logistic Centers and will provide engineering data and process information to allow each user to design and implement a systems and processes which will meet their specific requirements.

Potential users will be an integrated part of the R&D team so that their inputs will be incorporated on a continuous basis into the product development cycle.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	350	1050	1050	2450

12. Performers:

The project will be performed under the technical leadership and direction of:

Air Force Material Command
Aeronautical Systems Center
Wright Laboratory, Materials Directorate
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio.

13. Principal Investigator:

T. J. Reinhart
WL/MLSE
2179 12th Street, Suite 1
Wright, Patterson AFB, OH 45433
TEL: (513) 255-3691
FAX: (513) 476-4419

14. Keywords:

Cleaning, Coating, Adhesive bonding, VOCs, Ozone depleting substances, Non-aqueous cleaning media

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Large Aircraft Robotic Paint Stripping (LARPS)

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory, Manufacturing Technology Directorate

5. **Proposal ID:** #134

6. **Problem Statement:**

The Air Logistics Centers primary method to remove organic coatings from aircraft structures is with methylene chloride based chemical stripping compounds. Protective coatings for large aircraft primary and secondary structures consists of thin skin metallic and composite materials which must be removed by environmentally clean processes. The disadvantages of chemical paint stripping are: long processing time, expensive and hazardous chemicals, personnel exposed to hazardous environment, chemicals cause premature degradation of the working areas, and special disposal techniques are required to minimize environmental impact. Methylene chloride and other hazardous chemicals will be banned by the Air Force in 1997 and the Environmental Protection Agency, or federal law by the year 2000. An environmental safe, high pressure water system, is currently being developed as a Air Force Manufacturing Technology (MANTECH) project. This effort address thin skin metallic structures and composite components, but not aircraft radomes. The composite work requirements need to be expanded for radomes. However, radomes must conform to more stringent performance criteria to ensure accurate initial launch coordinates for missiles, artillery, and safe terrain avoidance/mapping information. Depot radome repairs consist of removing or "stripping" multi-layer dielectric coatings, filling and smoothing voids in the radome wall, and then applying new dielectric coatings on to the radome surface. Currently, there are four different coating systems that are applied to aircraft radomes. The overall technical effort of the LARPS will be expanded to address radome coating removal needs. Development actions for large aircraft primary and secondary structures manufactured from thin skin aluminum and composite structures will be continued. This is a previous FY92 SERDP funded program.

7. **Project Description:**

This project enhances the benefits and capabilities of the current Manufacturing Technology Directorate's LARPS program. The LARPS technology is evolving and the system is being developed, but has not yet been demonstrated. This initiative provides an enhanced, fully automated LARPS system providing an environmentally safe (94% reduction in hazardous waste) paint stripping system which will eliminate personnel exposure to a hazardous working environment. The current development work will be expanded to address composite radome structures. Additionally, the application of medium and high pressure water with various nozzle applications shall be incorporated into existing program requirements. The LARPS high pressure system is planned for KC-135, B-1 and E-3 aircraft applications. Additionally, this effort will address system refinements and expand its application for B-2 and B-52 aircraft. The technical risks are moderate.

Tie to Tri-service Environmental Quality R&D Strategic Plan
Pillar Thrust Area: 3.B.2
Requirements Category: 1.5
Work effort: Tech Demo

8. Expected Payoff:

This project eliminates significant quantities of hazardous chemical waste, reduces ALC personnel exposure to hazardous waste environment, and provides high estimated cost savings. The projected savings or cost avoidance is estimated to be $5.1 million/yr ($4.6M for aircraft structures and approximately $500,000 for radomes). This is a high priority project to significantly reduce hazardous waste, personnel exposure to a hazardous environment, cost, and aircraft production flow time.

9. Milestones:

1. Contract award 09/91
2. Complete detailed design 02/92
3. Complete aircraft system fabrication 04/95
4. Complete aircraft development & prototype 08/95
5. Complete test, production demonstration, qualification, and tech report (aircraft) 12/95
6. Begin technology transition to DoD and industry (aircraft structures) 01/96
7. Complete radome system development & prototype 12/96
8. Complete radome system demonstration, qualification, and tech report 12/97
9. Begin technology transition to DoD and industry (radome) 12/97

10. Transition Plan:

This technology will be demonstrated for initial aircraft production application at the Oklahoma City Air Logistics Center (OC-ALC). The technology transfer benefits have wide application for other DoD maintenance centers and the commercial airlines who must transition to chemically free or less hazardous coating removal systems by the year 2000 or earlier if possible.

11. Funding: ($K)

	PRIOR	FY94	FY95	FY96/97	TOTAL
SERDP	950	1940	0	0	2890
MANTECH	2950	1724	305	300	5279
OC-ALC	2529	1141	0	0	3670
FACILITY	508	0	0	0	508
SITE PREP	1600	0	0	0	1600
ACFT COMP	999	0	0	0	999
NAVY	999	0	0	0	999
TOTAL	10024	4805	305	300	15945

12. Performers:

The Wright Laboratory, Air Force Manufacturing Technology Directorate will provide technical and contractual management for this program and work in close coordination with the Navy and the OC-ALC. The current contractual effort is being developed by Pratt & Whitney Waterjet Systems, Huntsville, AL, the winner of a competitive AF contract to design and develop the aircraft system for potential DoD and industry applications. The radome coating removal system will be incorporated into existing contract requirements. The system will be demonstrated at Oklahoma City Air Logistics Center. This is a dual use technology applicable to commercial and military aircraft requirements.

13. Principal Investigator:

Mr. Dan Brewer
WL/MTAP
Building 653, Area B, 2977 P Street - Suite 6
Wright Patterson AFB, OH 45433-7739
TEL: (513) 255-3701 x 208
DSN: 785-3701 x 208
FAX: (513) 476-1268

14. Keywords:

Robotics, High pressure water, Paint removal, Methylene chloride, Hazardous waste, Phenols

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Laser Cleaning and Coatings Removal

3. **Agency:** Air Force

4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center

5. **Proposal ID:** #139

6. **Problem Statement:**

The goal of the proposed effort is to provide a field demonstration of a prototype laser-based facility to demonstrate environmentally acceptable component cleaning and coating removal technology and to transition it to aerospace users, including the following the Air Force Logistic Centers:

Oklahoma City Air Logistics Center (OC-ALC)
San Antonio Air Logistics Center (SA-ALC)
Warner Robbins Air Logistics Center (WR-ALC)
Sacramento Air Logistics Center (SM-ALC)
Ogden Air Logistics Center (OO-ALC)

Cleaning and coatings removal technologies have traditionally depended upon the use of organic solutions, such as, PD 680 (I, II, & III) methyl ethyl ketone (MEK), methylene chloride (MECL), phenol, and strong acids and bases as well as hot potassium permanganate solutions. These materials are hazardous, and include volatile organic compounds (VOCs), ozone depleting chemicals (ODCs) and air toxic emitters which are subject to severe restrictions or are being banned altogether, such as freon (CFC-113). More recently, the trend in cleaning technology is toward the use of water based cleaners (sodium metasilicate, bases, terpene/water emulsions or water detergent blends), some of which may be hazardous to some degree. However, technologies are needed which do not involve generation of waste water streams.

Laser-based cleaning and coating removal has been demonstrated to be an environmentally acceptable, affordable and controllable technology. A demonstration facility is needed to facilitate transition of this technology to Air Force, DoD and industry use, targeted to the immediate needs of the Air Logistics Centers.

This is the continuation of an FY93 SERDP funded program.

7. **Project Description:**

The project objective is to demonstrate the use of laser cleaning and coating removal on components ranging from turbine engine blades to landing gear and radomes.

The project approach is to design, fabricate test, evaluate and demonstrate a state-of-the-art automated, controllable laser cleaning and coating removal facility. The facility will be designed for carbon dioxide and eximer laser cleaning and coating removal operations. System operation

will be fully robotized and computer controlled with on-line instrumentation for component positioning and measuring and controlling laser inputs to the part surfaces.

The project involves the following tasks:

Design system to demonstrate technology on fighter aircraft landing gear and radome components.

Design a subsystem system to handle, treat or capture, as necessary, all gaseous and particulate products of the process.

Purchase or fabricate lasers, computers, robotics, controller, sensors, hardware and software necessary for the operation of the system.

Assemble the demonstration facility system. Make necessary mechanical hardware and software modifications to insure safe, reliable and controllable operations.

Demonstrate system on both metallic and non-metallic specimens.

Test and evaluate adequacy of cleaning and coating removal process for aircraft components.

Operate the facility and make it available for ALC and GOCO engineering evaluation on specific aircraft components.

Qualify facility to applicable specifications for aircraft components cleaning and coating removal.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort also will enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment. This program supports the DoD objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

Extensive test and evaluation work has been completed by the Air Force and the Navy on laser radiation effects on substrate materials and coating removals. What is needed next is a prototype facility where test and evaluation cost analysis and cleanliness levels can be performed on a variety of aircraft components. The facility would be available to the services as well as the aerospace community for test and evaluation purposes.

The technical risks involved in this project are low. Industrial lasers, both carbon dioxide and eximer are available; controls, robotics sensors, instrumentation are also available. Software will have to be developed/modified to control the production system. Systems design must incorporate all applicable safety devices and features.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area:	3.B.2
Requirements Category:	3.I.5.a
Work effort:	Tech Base

8. Expected Payoff:

The laser based cleaning and coating removal facility will be applicable to a broad range of aircraft and general equipment cleaning and coatings removal work. Benefits include the complete elimination of the use of toxics and hazardous waste generation in logistic center maintenance and re-manufacturing operations relying on the new technology. The limits of such potential payoff is presently unexplored and still remain to be determined. The process is expected to be highly cost effective considering that all costs for hazardous materials management and management of solid, liquid, and vapor waste streams will be eliminated.

9. Milestones:

1.	Project Initiation/start Initiate preliminary systems requirements study	07/93
2.	Complete preliminary systems requirements study	09/93
3.	Complete detailed systems analysis design Initiate design review process	12/93
4.	Approve Design - Initiate hardware procurement/component fabrication	03/94
5.	Initiate life cycle cost study	05/94
6.	Initiate systems assembly and check-out operations	08/94
7.	Complete check-out and de-bug of system operations	10/94
8.	Initiate test and evaluation with services and industry customers	12/94
9.	Complete life cycle cost studies and economic benefit studies	08/95
10.	Final report and transfer of system to selected ALC	09/95

10. Transition Plan:

It is planned that the system to built under this effort will be a prototype demonstration and as such will have many more capabilities than required on an actual production system. Users will perform test and evaluation programs on the prototype and determine the capabilities needed for their production unit. Cost data will be generated, specific engineering problems will be addressed and production systems design requirements will be generated.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	300	2100	2100	4500

12. Performers:

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate, Wright-Patterson AFB, OH 45433.

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

13. Principal Investigator:

T. J. Reinhart
WL/MLSE
Wright-Patterson AFB, OH 45433-6703
TEL: (513) 255-3691
FAX: (513) 476-4419

14. Keywords:

Cleaning, Coating removal, Lasers, Methylene chloride, Methyl ethyl ketone, Phenols

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Aircraft Depainting Technology

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division Warminster

5. **Proposal ID:** #081

6. **Problem Statement:**

To develop a non-hazardous replacement for chemical paint stripping use on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Current chemical paint strippers contain hazardous components like phenols, methylene chloride and chromates. Paint removal operations at maintenance depots has been determined to be a major contributor to hazardous waste generation in the DoD. Federal agencies like the EPA and state agencies like the California Air Quality Management Districts (AQMD) have begun to restrict the use of these hazardous materials. Regulations like the Clean Air and Water Acts, CERCLA, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, OPNAV and CNO directives require significant reductions in hazardous waste generated by the Navy. Several generic alternative stripping methods to the present chemical removers are being developed. These techniques need to be optimized and evaluated for use at Naval Aviation Depots. Therefore, to comply with existing and future regulations while maintaining aircraft performance and operational readiness, these alternative methods need to be investigated. This effort is covered under the Tri-Service EQ Strategic Plan: Pillar 3 Pollution Prevention, Requirement Thrust: 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

7. **Project Description:**

Alternative methods of coating removal that meet increasing waste disposal constraints, have to be developed to maintain aircraft rework operations while reducing hazardous waste generation. Because there are so many different substrates/alloys and coating systems currently used by the Navy, these non-hazardous paint removal processes will also have to be versatile. Naval aircraft have different load bearing structures (higher strength) to withstand aircraft carrier landings. In addition, the Navy's operational environment can have a seriously deleterious effect on the structural integrity of aircraft skins. This issues complicate the stripping process for naval aircraft. This program will identify the best alternatives from existing and developmental methods such as non-hazardous chemical paint strippers (i.e. materials that do not contain chromates, methylene chloride, phenol, etc); enzymatic strippers; and mechanical removal procedures (PMB, flash lamp, UV, dry ice stripping, water jet stripping, etc). Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. Comparison of techniques as well as advantages/disadvantages will also be performed. Mechanical removal procedures eliminate the use of hazardous chemicals, however, several individual mechanical techniques damage the substrate surface during the removal process. Since some sections of aircraft skins are very thin, this is not acceptable. However, if several techniques are combined

to remove the coating the surface damage could be eliminated/minimized to an acceptable level. For example, one possible combination is flash lamp/dry ice stripping. The flash lamp would degrade the coating system and the dry ice stripping perform the final removal at a reduced pressure (i.e. reduced surface damage). Finally, the treatment of the blast media used in these mechanical techniques will be investigated for waste reduction.

8. Expected Payoff:

The elimination of the majority of chemical paint strippers would significantly reduce the total amount of hazardous materials generated by the Navy. Furthermore, requirements for emission control equipment for methylene chloride (estimated at $1M/facility) would be eliminated. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reducing handling and waste disposal costs, Navy aircraft and equipment will be properly maintained. This is particularly important considering the cost of these A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to many areas of the commercial sector (aerospace, automotive, marine, etc).

9. Milestones:

1.	Evaluate Alternative Stripping Processes' Parameters	09/92
2.	Characterize Enzyme System Activity/Stability	09/92
3.	Establish Joint Navy/Air Force Investigation of FlashJet	09/92
4.	Optimize Alternative Depaint Processes (I Level)	06/93
5.	Evaluate Plastic Blast Media Treatment Processes	09/93
6.	Select Genes for Enzyme Synthesis	09/93
7.	Evaluate Flash Lamp/Dry Ice Combination Stripping (Joint Navy/ Air Force Program)	11/93
8.	Service Demonstration of Optimized Alternative (I Level)	06/94
9.	Service Demo Plastic Blast Media Treatment Processes	06/94
10.	Evaluate water-jet stripping	09/94
11.	Optimize Flash Lamp/Dry Ice Combination Stripping (Joint Navy/ Air Force Program)	12/94
12.	Production of a Batch of Enzymes for Stripper Studies	03/95
13.	Implement Optimized Alternative (I Level)	06/95
14.	Implement Plastic Blast Media Treatment Processes	06/95
15.	Optimize water-jet stripping	09/95
16.	Service Demonstration of Flash Lamp/Dry Ice Combination (Joint Navy/ Air Force Program)	12/95
17.	Conduct Enzyme Stripping Studies	06/96
18.	Service demo of water-jet stripping	06/96
19.	Implement Flash Lamp/Dry Ice Combination Stripping (Joint Navy/ Air Force Program)	09/96
20.	Evaluate/Optimize Enzyme Stripping	06/97
21.	Implement water-jet stripping	09/97
22.	Service demo Enzyme Stripping	09/98
23.	Implement Enzyme Stripping	12/98

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP in coordination with the Lead Maintenance Technology Center for Environment and the National Defense Center for Environmental Excellence (WaterJet & hand held flashjet). These processes will be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials and processes will insure availability for implementation.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
NAYY	--	--	185					185
DERA	130	250						380
SERDP	261	35	445	950	930	855	610	3345
TOTAL	391	285	630	950	930	855	610	4651

12. Performers:

Development of alternative stripping processes is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Research Laboratory, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. This effort is being coordinated with efforts being performed by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB) and aerospace industry (MDA-E, Boeing, etc.). The University of Maryland (Bioreactor scale-up facility) will collaborate with the enzymatic stripping effort.

13. Principal Investigator:

Stephen J. Spadafora
Naval Air Warfare Center Aircraft Division Warminster
P.O. Box 5152 (Code 6062E)
Warminster, PA 18974-0591
Phone: (215) 441-2704
FAX: (215) 441-1925

14. Keywords:

Paint stripping, Materials Substitution, Waste Recycling/Reuse, Flashjet, Waterjet, Enzymatic Paint Degradation

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycle Boiler Nitrite Solution

3. **Agency:** Navy

4. **Laboratory:** Naval Facilities Engineering Service Center (NFSEC; formerly Naval Civil Engineering Laboratory (NCEL))

5. **Proposal ID:** #069

6. **Problem Statement:**

The nitrite solutions used for marine boiler tube hydroblast, lay-up, hydrostatic testing, and rinsing must be recycled to the extent possible and then treated for NPDES disposal with minimal nitrate conversion. The Navy uses nitrite extensively as a rust-preventing fluid in marine boiler maintenance. Because it oxidizes readily to nitrate, it will support surface water eutrophication and is therefore treated as a "de facto" hazardous waste regardless of whether contaminants are taken up in its usage. This has resulted in high disposal costs.

NFESC has been working on this problem since FY90 and has developed a highly successful treatment process, based on sulfamic acid, that converts nitrite to nitrogen gas with little or no conversion of the nitrite to nitrate being caused by the treatment itself. Working with the Naval Station, Treasure Island, CA, it has been determined that the nitrite solutions can be recycled a number of times as long as they are stored under an oxygen free head gas and are treated and disposed of before the nitrate concentrations acquired from hydroblasting, lay-up or hydrostatic testing do not reach unacceptable levels. The challenge now is one of bringing these technical requirements into a cost-effective and dockside acceptable system that will eliminate the need for exporting nitrite wastewater.

This is an enhancement to an on-going 6.3 technology demonstration project. It addresses SERDP Thrust 3.A.2.b: Metal working Process/cleaning & Degreasing, and it supports a SERDP goal to minimize or eliminate hazardous wastes at the source.

7. **Project Description:**

The goal of this project will aim at: (1) full scale design and demonstration testing of the sulfamic acid process at a selected Naval shipyard; (2) designing an oxygen-exclusive, conditioning process for bringing the used nitrite solutions back to specification quality; (3) development of a practical procedure for long-term storage of recyclable nitrite solutions without head-gas caused nitrate formation; and (4) evaluation of an alternative biological treatment process suggested by EPA.

Full scale sulfamic acid process demonstration will be accomplished preferably at the Long Beach Naval Shipyard using the NFESC plant that was erected there and successfully tested in FY92. This will be an operational demonstration using shipyard personnel and nitrite wastewater solutions from ship(s) being serviced there. Samples will be taken to fully characterize the wastewater before and after denitrification process. These data will be used to determine the

processing necessary to restore the liquid to specification quality. Previous data obtained by NCEL show that reconstitution should be quite practical. A system will then be designed, fabricated, and tested. The final process step will be the design of a system that will permit the oxygen-free storage of the reworked nitrite solution. Operating procedures will then be defined that will govern the use of the nitrite solution in a manner that will ensure extended cycles of service.

The Risk reduction Engineering laboratory of EPA, Cincinnati, will team with NFESC on this effort. Their primary interest is to evaluate a biological system that will convert both nitrite and nitrate to nitrogen gas. If such a process proves successful, it would greatly extend the useful cycles before disposal is required and significantly reduce the costs entailed in chemical treatment.

The technical risk is very low. The project addresses Tri-Service Environmental R&D Strategic Plan, Requirement (I.2.b): Non-polluting, Non-toxic Cleaning and Degreasing Technology.

8. Expected Payoff:

Take Long Beach Naval Shipyard as an example, the average cost of disposing of the approximately 500,000 gallons of nitrite wastewater generated annually is about $1,500,000 at $3.00/gallon.

After successfully implementing the NCEL hydroblast recycling process, it has been estimated that the total volume of sodium nitrite wastewater generated by all Naval shipyards to still be about 3 million gallons each year, and by Navy-wide boiler maintenance operations to be 10 million gallons per year. The proposed chemical denitrification process has the potential of reducing the disposal cost by at least 90 percent (reduced from $3.00/gallon to $0.30/gallon operating cost) or $8M savings per year for Naval shipyards and $17M savings per year for the Navy-wide boiler maintenance operations.

The proposed chemical process will not produce hazardous waste and the effluent produced can be safely discharged to the sanitary sewer.

This project should have very high transition opportunities because of the high payoffs.

9. Milestones:

1.	Complete Test & Evaluation Plan and permit application at test site	3/95
2.	Complete full scale denitrification process design & fabrication	6/95
3.	Complete full scale demonstration	12/95
4.	Complete design, fabrication, and testing of nitrite recycle system	3/96
5.	Complete development and testing of nitrite storage procedure	6/96
6.	Complete evaluation of a biological system converting nitrite/nitrate to nitrogen gas	6/96
7.	Complete development of User Data Package and final reports	9/96

10. Transition Plan:

At the conclusion of this project, the proven full-scale demonstrated system will be left at the host site for continuous operation. Implementation throughout the Navy will be done through the cooperation with Naval Ship Systems Engineering Station (NAVSSES). The technology transfer documentation (User Data Package) will be published as a final deliverable. This UDP will contain information on system design & specification, O&M, permitting, training, and safety plan. The other DoD agencies and private industry will have access to the information developed and, with it, will be able to apply the technology thus described as desired.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	475	150	100	725

12. Performers:

NAVY/NAVSEA/NFESC and EPA. The Risk Reduction Engineering Laboratory of EPA, Cincinnati, will team with NFESC on this effort and has proposed to the SERDP Executive Director the evaluation a biological system that will convert both nitrite and nitrate to nitrogen gas.

13. Principal Investigator:

Dr. Richard Lee, Code ESC421
Naval Facilities Engineering Service Center
560 Center Drive
Port Hueneme, CA 93043-4328
TEL: (805) 982-1670
FAX: (805) 982-1409

14. Keywords:

Nitrite, nitrate, denitrification, sulfamic acid, nitrogen gas, boiler

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Acid Recycle

3. **Agency:** Department of Energy

4. **Laboratory:** Los Alamos National Laboratory (LANL)

5. **Proposal ID:** #422

6. **Problem Statement:**

Field demonstrations will be conducted at the Los Alamos Plutonium Facility to recycle and reconcentrate nitric and hydrochloric acids from plutonium-containing liquid waste streams.

Nitric acid and hydrochloric dissolution of plutonium-containing solids is a baseline technology for Complex 21 plutonium processing operations. Following removal of plutonium from the acid solutions, previous operations neutralized the acid with caustic and discarded it as waste. Most of the nitric or hydrochloric acid could be separated from the waste solutions and recycled, thus reducing amount of waste generated. This in process technology can also provide major reductions in nitrates and chlorides in effluent streams from processing aimed at cleanup of residues from previous operations.

Recycle of nitric acid will be accomplished via an enhancement of capabilities in the ATLAS (Advanced Testing Line for Actinide Separations) integrated process system. Recycle of hydrochloric acid represents a new program to be implemented using the Los Alamos EXCEL (Experimental Chloride Extraction Line) system.

7. **Project Description:**

We will demonstrate at least 95% recycle of nitric and hydrochloric acid from waste solutions. The recycle acid will be reconcentrated sufficiently to be used for dissolutions, etc. in lieu of makeup acid.

We will demonstrate nitric and hydrochloric acid recycle from actual plutonium processing waste solutions using two operations:

(1) evaporation of acid from a solution containing radionuclides and inorganic salts and (2) fractional distillation of evaporator product to generate concentrated acid. The acids will be separated from the radioactive component of the waste solution by evaporation. The nonvolatile radioactive residue will be sent to disposal or may receive further treatment (e.g., thermal denitration) before disposal. Evaporated acid will be reconcentrated to a reusable state by fractional distillation. We will develop an integrated process using semi-continuous operation consisting of an evaporator followed by a distillation column.

The existing nitric acid evaporator in the ATLAS system will be operated for additional experience. A nitric acid distillation column will be designed, built, and cold-tested prior to incorporation into ATLAS. Process flow balance and characterization of hydrochloric acid

processes will be done. Bench-scale, "cold" evaporation and distillation experiments will be done on hydrochloric acid solutions. An evaporator and a distillation column for hydrochloric acid recycle will be designed, built, and tested. Hydrochloric acid recycle apparatus will be installed and integrated into the EXCEL operation.

Present nitric acid waste solutions from plutonium processing contain both amounts and concentrations of nitrates far above desired levels to meet environmental objectives. Potentially leaching of soluble salts (nitrates and chlorides) from cemented radioactive wastes is an unknown which raises major concern. It is very desirable to reduce quantities of TRU wastes to a minimum. Acid recycle promises to provide significant relief in each of these areas.

Nitric acid recycle by evaporation and distillation has been used in uranium operations at Y-12. Savannah River Site has recovered and reconcentrated nitric acid as part of their operation. Pacific Northwest Laboratories has built pilot-scale apparatus for potential acid recycle use at Hanford. New Los Alamos work using freeze-drying for decontamination of nitric acid waste solutions could be integrated with this work.

Recycle of both nitric and hydrochloric acid presents no major technical risks. Evaporation and fractional distillation are both mature technologies. While these have not been applied to recycle of plutonium waste solutions as integrated processes, much industrial production of nitric and hydrochloric acids use this approach.

8. Expected Payoff:

Applicability: Complex 21 processing of plutonium; cleanup of previous plutonium processing residues

Benefits:
- Reduced number of waste units requiring handling, inspection, packaging, shipping, storage, etc.
- Major reduction in waste disposal costs
- Acid reagent costs reduced
- Potentially leachable nitrates, chlorides in waste reduced

Capability: At least 95% of the acid will be recycled. Acid concentrations will be sufficient for reuse in processing.

Cost-savings example based upon previous Rocky Flats operation:
- Total saltcrete production reduced by 50%
- Waste disposal costs reduced by $12M/year
- Nitric acid reagent costs reduced by $100K/year

9. Milestones:

1.	Complete cold tests of HNO_3 distillation column	8/95
2.	Install HNO_3 column in ATLAS; connect to evaporator	7/96
3.	Characterize HCl wastes; make flowsheet balances	8/95
4.	Conduct bench-scale HCl experiments	9/96
5.	Conduct HNO_3 recycle demonstrations using evaporation and distillation column	9/96
6.	Design HCl evaporator and distillation column	9/96

7. Build HCl evaporator and distillation column 9/96
8. Conduct cold tests of HCl evaporator and distillation column 9/96
9. Begin HNO_3 recycle upgrades (e.g., freeze drying,denitration, NO_x handling) 9/96

10. Transition Plan:

Following successful demonstration of acid recycle in ATLAS and EXCEL, acid recycle will be applied to all acid effluents from the Plutonium Facility at Los Alamos. Previous nitric acid effluent solutions have amounted to 75,000 L/year. Hydrochloric acid processing has had limited prior use. Both performer and user are the same. No industrial participation is foreseen.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	258	375	283	0	916
DOE	0	0	0	0	0	0
TOTAL	0	258	375	283	0	916

12. Performers:

Department/Agency Laboratory: Los Alamos National Laboratory will conduct the work.

Industry involvement: No industrial involvement is foreseen at present. There has been previous collaboration with the Colorado School of Mines.

Planned cooperative development agreements: There are no planned cooperative development agreements.

13. Principal Investigator:

Thomas R. Mills
Group NMT-6 MS E510
Los Alamos National Laboratory
Los Alamos, NM 87545
Phone: (505) 665-0631
FAX: (505) 665-4459

14. Keywords:

recycle, reconcentrate, acid, plutonium, nitric, hydrochloric, effluent

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Capacitive Deionization for Elimination of Wastes (Renewal)

3. **Agency:** United States Department of Energy (DOE)

4. **Laboratory:** Lawrence Livermore National Laboratory (LLNL)

5. **Proposal ID:** #436

6. **Problem Statement:**

Background: Ion exchange is used to remove anions and cations, including heavy metals and radioisotopes, from aqueous streams at Department of Energy (DOE) and Department of Defense (DoD) facilities, as well as at a variety of civilian industrial plants. Such deionization processes generate large volumes of corrosive secondary waste that must be treated, including spent anion and cation exchange resins, and acids and bases contaminated during regeneration. Solutions of H_2SO_4 are used for the regeneration of cation columns in metal finishing and power industries, while HNO_3 is used for regeneration of cation columns in plutonium processing plants. During plutonium processing, resins and solutions of HNO_3 become contaminated with PuO_{2++} and other radioisotopes. Every pound of cation exchange resin requires approximately 100 lb of 10 wt. % $H2SO_4$ or HNO_3 and 2-3 lb of rinse water for regeneration. Solutions of NaOH are used to regenerate anion exchange resins. Given the high cost of disposal in mined geological repositories, there is tremendous incentive for reducing the volume of waste that must be dealt with.

Objective: The objective of this project is to develop an innovative new technology, capacitive deionization, that can be used to replace many existing ion exchangers, thereby eliminating the secondary wastes due to regeneration. In this novel process, ions are retained in the electric double layers formed at the surfaces of two porous electrodes of opposite polarity. Such technology could also be used to treat ground water, surface water, waste water, drinking water, boiler water for power plants, and process water for semiconductor manufacturing. Deionization of boiler water is used as a means of preventing fouling and corrosion of heat transfer surfaces. It may even be possible to use capacitive deionization for the energy-efficient desalination of sea water. In FY93, work has been focused on proof of principal. We propose to build a continuous-flow pilot plant during the second year, FY94.

7. **Project Description:**

Principal of Operation. The capacitive deionization process uses a porous-electrode flow-through capacitor to remove cations and anions from water. Conceptually, the construction and operation of this process is relatively simple. Two porous electrodes with high specific surface area are fabricated from carbon aerogel (or carbon powder) and separated by either a cation exchange membrane or a dielectric microporous sheet. Ions are forced to move to the surfaces of electrodes by an imposed electric field. Cations are concentrated in the electric double layer formed at the surface of the cathode, while anions are concentrated at the surface of the anode. A cation exchange membrane such as Nafion 117 could be used as the electrode separator in a design that is similar to that of the LLNL Aerocapacitor. During the deionization of a NaCl

solution with such a device, protons migrate through the ion exchange membrane to balance the anodic charge associated with Cl^- anions, thereby forming HCl. Since H^+ will also populate the electric double layer formed at the cathode, the presence of HCl in the cathode compartment will reduce the removal efficiency for other cations such as Na^+. A better design uses a dielectric microporous membrane that allows diffusion of both cations and anions, thereby preventing the formation of HCl. Separators that allow bipolar transport are more desirable than ion exchange membranes.

Innovative Aspects: Capacitive deionization is a novel and innovative alternative to ion exchange. The electrode material and proposed mode of operation are entirely new. Carbon aerogels have much higher specific surface areas (600-900 m^2/gm) than conventional carbon-paste electrodes or activated carbon powders (200-300 m^2/gm). By using carbon aerogel as the electrode material, instead of carbon paste or powder, the capacity of the deionizer will be increased dramatically (3X). Note that carbon aerogel was developed by Lawrence Livermore National Laboratory (LLNL) and is a "spin-off" of the Strategic Defense Initiative (SDI) Program. Therefore, this project makes use of a technology developed for national defense purposes. The continuous-flow potential-swing mode of operation to be developed during FY94 is also novel.

Theoretical Model of Capacitive Deionizer: In addition to process development and demonstration, computer models are being developed that can be used for computational analyses, engineering scale-up, and parametric optimization. Parameters that are being studied include: (1) electrode porosity and thickness; (2) separator porosity and thickness; (3) superficial fluid velocity; (3) charging voltage; and (4) number of electrodes (stages). The original theory for porous-electrode flow-through capacitors was developed by Prof. John Newman of U. C. Berkeley [J. Electrochem. Soc. 118, 3 (1971) 510-517].

FY93/Proof of Principle. The effluent from a single capacitive deionizer is being monitored with an on-line conductivity probe, as well as various ion-selective electrodes, and recorded with a strip-chart recorder and/or computerized data acquisition system. This array of sensors is being used to determine removal efficiencies and selectivities for various anions and cations in multicomponent electrolytes. Measured effluent concentrations will be compared to predictions for model validation.

FY94/Continuous-Flow Pilot Plant. A continuous-flow pilot plant will be built that consists of two parallel multistage capacitors. This system will be inherently energy efficient since the current from the discharge of one capacitor will be used to charge the other. One unit will be regenerated (discharged) while the other purifies (charges). This mode of operation will be called potential-swing ion adsorption and is analogous to pressure-swing gas absorption. On-line sensors will also be used to monitor conductivity, pH, and concentrations of cations and anions in the pilot plant. A computer will be used to log data, control flow, and synchronize the charge-discharge cycles of each capacitor.

8. Expected Payoff:

This project will minimize waste generation at the source by substituting nontoxic and nonpolluting electricity for the acids and bases that are normally used for regeneration of ion exchange resins. The Pollution Prevention Act of 1990 states that "pollution prevention" means "source reduction" and other "practices that reduce or eliminate the creation of pollutants through: increased efficiency in the use of raw materials including energy, water, and other resources; or materials substitution. In capacitive deionization, we are substituting porous

carbon electrodes for ion exchange resins and are substituting electrical current for the chemicals that are normally used to regenerate resins. We believe that this process will reduce the total volume of solid waste from water treatment that will have to be disposed of. Consequently, this process will help extend the life of existing landfills, geological repositories, and other disposal facilities. This innovative process may also prove to be an innovative remediation technology for sites contaminated with heavy metals, radionuclides, and other inorganic contaminants. Ultimately, it may be possible to use this technology as an efficient and effective means of ground water and surface water cleanup.

9. Milestones:

1. Development of computational model	12/93
2. Design of proof-of-principle capacitive deionization system for batch processing	01/94
3. Procurement of vessels, valves, pumps, power supplies, conductivity monitors, ion selective, electrodes, and strip-chart recorders	02/94
4. Preparation of large quantity of carbon aerogel	03/94
5. Measurement of surface charge density of carbon aerogel electrodes as a function of electrolyte composition and potential	04/94
6. Construction of proof-of-principle capacitive deionization system	05/94
7. Testing of fluid flow systems	06/94
8. Testing of electrical and electronic systems	06/94
11. Determine efficiencies for removing ions from symmetric (z:z) electrolytes	07/94
12. Verification and continued development of model	08/94
13. Documentation of FY93 progress	09/94
14. Determine process efficiency for more complicated and more realistic electrolytes	12/94
15. Design of pilot-scale capacitive deionization system for continuous operation	03/95
16. Procurement of additional vessels, valves, pumps, power supplies, conductivity monitors, and ion selective electrodes, as well as equipment for computer control	06/95
17. Preparation of additional carbon aerogel on corrosion-resistant supports	06/95
18. Construction of pilot-scale capacitive deionization system for continuous operation	09/95
19. Documentation of progress during second year	09/95
20. Testing of fluid-flow systems	10/95
21. Testing of electrical and control systems	11/95
22. Testing of entire system with symmetric electrolytes	12/95
23. Determination of selectivities and removal efficiencies with more complicated, multicomponent electrolytes	06/96
24. Demonstration of system with actual streams	09/96
25. Investigate deployment within DOE and DoD	06/97
26. Technology transfer into the private sector	09/97

10. Transition Plan:

After a working prototype process is developed, the technology will be made available to engineers who are working on reconfiguration of the DOE Complex. In collaboration with these engineers, tests will be conducted to determine where capacitive deionizers can be used to replace conventional ion exchangers. This new technology will also be important in the private sector. As previously discussed, a capacitive deionizer could be used to produce deionized feed water for boilers in fossil-fired and nuclear power plants. In the future, it may be possible to use such novel technology for the energy-efficient desalination of water for dry, heavily-

populated areas like California. Deionized water, free of dissolved organic resin, could also be used for the manufacture of next-generation semiconductors (nanoelectronics). Nanoelectronics will be far less tolerant of impurities introduced by beds of ion exchange resin than microelectronics. This concept (capacitive deionization) was presented to senior level executives of Dow Chemical Company during one of their recent visits to LLNL. They expressed a sincere interest in working with LLNL in a Collaborative Research and Development Agreement (CRADA). It is noteworthy that the Principal Investigator for this project also served as the Principal Investigator for another electrochemical waste treatment project that resulted in the development of technology that has been licensed to a small business in the San Francisco Bay Area.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	795	700	200	0	0	1695
DOE	0	200	600	800	300	1900
TOTAL	795	900	800	800	300	3595

12. Performers:

LLNL is a DOE laboratory operated by the University of California and will be responsible for successful completion of the proposed work. This laboratory has recently developed several novel electrochemical processes for the treatment and destruction of mixed wastes [J. C. Farmer et al., J. Electrochem. Soc., 139, 3 (1992) 654-662; Trans. Inst. Chem. Engr., 70B (1992) 158-164; J. Electrochem. Soc., 139, 11, (1992) 3025-3029]. Several patent disclosures have been filed and are being actively pursued by the U. S. Department of Energy. Carbon aerogels with very high surface areas have also been developed by LLNL [R. W. Pekala et al., J. Non-Crystalline Solids, 145 (1992) 90-98]. These materials have unusually high specific surface areas of 600-900 m^2/gm, much higher than the 200-300 m^2/gm that is typical of activated carbon powder. LLNL has developed electrolytic supercapacitors for energy storage applications that have carbon aerogel electrodes (known as Aerocapacitors). These new energy storage devices have energy densities of 4-25 Whr/kg, power densities of 0.1-10 kW/kg, and cycle lives greater than 100,000, and are now believed to be essential for load-leveling applications in electric vehicles. As previously discussed, the theory for flow-through porous-electrode electrolytic capacitors was developed and published by Newman over 20 years ago. Little or no work has been done in this area since that time.

13. Principal Investigator:

Joseph C. Farmer, Ph.D. L-352
Chemistry and Materials Science Department
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, California 94550
Phone: (510) 423-6574 FAX: (510) 422-6892

14. Keywords:

Deionization, ion exchange, waste minimization, supercapacitor, aerogel, potential-swing, capacitive deionization.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Alternative Electroplating Technology

3. **Agency:** Navy

4. **Laboratory:** Naval Air Warfare Center Aircraft Division, Warminster

5. **Proposal ID:** #071

6. **Problem Statement:**

To replace hazardous plating processes (chromium, cadmium, cyanide, etc) currently used on Naval aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Chromium and Cadmium are heavy metal pollutants and carcinogens. Cyanide is hazardous to human health. The Clean Air Act Amendment of 1990 (Electrolytic Chromium National Emission Standard for Hazardous Air Pollution (NESHAP), etc.) as well as other EPA and state Departments of Environmental Resources regulations restrict the emissions from these processes. In addition, OPNAV and CNO directives require reductions in hazardous waste. Presently, these plating processes are used in production and Depot level maintenance operations. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, alternative plating processes need to be developed and validated. This effort is covered under the Tri-Service EQ Strategic Plan Area: Pillar 3: Pollution Prevention, Requirement Thrust: 3.I.3 Metal Working/Plating and Finishing (e-h) and is a continuation of an existing SERDP 6.2/6.3 effort.

7. **Project Description:**

Chrome plating and cadmium plating are common inorganic corrosion preventive coatings. Chrome plating is also used to build up worn components when they no longer meet tolerance levels. Cadmium plating is frequently used for fasteners and other very tight tolerance parts because of the dual qualities of lubricity at minimal thickness and superior sacrificial corrosion protection. Replacements for chromium and cadmium will require similar mechanical and performance properties over the full spectrum of applications for which they are currently used. Tin-zinc and zinc-nickel electroplating both offer potential to fulfill all of the requirements of Cadmium plating. These processes provide characteristics which would meet the majority of the corrosion resistance and lubricity requirements of Cadmium plating. A joint Navy industry effort will optimize and demonstrate this capability. Another alternative to Cadmium plating which has potential to fulfill all of these requirements is aluminum-manganese (Al-Mn) electroplating from a molten salt bath. This process differs from the traditional aqueous electrolytic plating bath. Optimum Al-Mn concentrations for Naval aircraft use will be isolated through a test program which examines the varied choices of Al-Mn systems on test coupons of various materials and sizes. This bath formulation will then be established as a full size prototype at a selected NADEP. Following full scale tests Al-Mn will be transitioned to the fleet through specification modification and design changes. In addition, ion vapor deposited (IVD) aluminum is another demonstrated alternative for certain applications that will be pursued for Navy use. Other alternatives to hexavalent chrome plating and cadmium plating that will be investigated include electroless nickel plating and hard chrome plating as well as alternative

application techniques with non-chrome/cadmium materials (physical vapor deposition, spray casting, flame spray/high velocity oxygen fuel, etc). Finally, cyanide strippers have been used to remove metallic coatings. Non-cyanide strippers will be evaluated based on an Air Force investigation.

8. Expected Payoff:

The elimination of chromium and cadmium plating significantly reduces the total amount of hazardous materials emitted from Navy operations. Elimination of chrome plating also eliminates the need for expensive emission control equipment required by CAA and AQMD legislation (estimated at several $M per Depot facility). Furthermore, these alternatives significantly reduce disposal costs of chromium and cadmium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial airlines and automotive industries, equipment manufacturers, fastener manufacturers, etc.

9. Milestones:

1.	Investigate IVD Aluminum for Specific Navy Applications	09/92
2.	Initiate Al-Mn Investigation	06/93
3.	Initiate Zinc-Nickel Electroplating Investigation	09/93
4.	Initiate Tin-Zinc Electroplating Investigation	09/93
5.	Evaluate Zinc-Nickel Electroplating	06/94
6.	Evaluate Tin-Zinc Electroplating	06/94
7.	Evaluation of Al-Mn Electroplating	09/94
8.	Electroless Ni Optimization/Demonstration	12/94
9.	Optimize Zinc-Nickel Electroplating	06/95
10.	Optimize Tin-Zinc Electroplating	06/95
11.	Optimization of Al-Mn Electroplating	09/95
12.	Implementation of Electroless Ni Electroplating	12/95
13.	Service Demonstration of Zinc-Nickel Electroplating	09/96
14.	Service Demonstration of Tin-Zinc Electroplating	09/96
15.	Demonstration of Al-Mn Electroplating	09/96
16.	Initiate Spray Casting Investigation	06/97
17.	Initiate Physical Vapor Deposition Evaluation	06/97
18.	Initiate Flame Spray/HVOF Process evaluation	06/97
19.	Implementation of Tin-Zinc Electroplating	09/97
20.	Implementation of Al-Mn Electroplating	09/97
21.	Investigate Non-Cyanide Metal Strippers	09/97
22.	Implementation of Zinc-Nickel Electroplating	09/97
23.	Optimize Spray Casting Process	09/98
24.	Service Demonstration of Non-Cyanide Metal Strippers	09/98
25.	Optimize Physical Vapor Deposition	12/98
26.	Optimize/demonstrate Flame Spray/HVOF Processes	12/98
27.	Implement Non-Cyanide Metal Strippers	09/99
28.	Service demo/transition Spray Casting Process	09/99
29.	Physical Vapor Deposition Service Demo/Transition	09/99

10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through coordination with the Lead Maintenance Technology Center for Environment. These processes will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials will insure availability for implementation.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	FY97	FY98	FY99
SERDP	138	460	360	550	400	730	350	350

12. Performers:

Evaluation/demonstration of Chromium and Cadmium Plating alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. The Cadmium replacement efforts (Zn-Ni & Sn-Zn) also have Boeing, Peter Gumm and McGean Rhoco as industry partners. This effort is being coordinated with the Air Force (Tinker ALC, Tyndall AFCESA), the Army and aerospace industries (Boeing, Grumann, MDA-E, etc.).

13. Principal Investigator:

Stephen J. Spadafora
Naval Air Warfare Center Aircraft Division Warminster
P.O. Box 5156 (Code 6062E)
Warminster, PA 18974-0591
Phone: (215) 441-2704
FAX: (215) 441-1925

14. Keywords:

Electroplating Processes, Materials Substitution, Chromium Replacement, Cadmium Replacement, Alternative Plating Technologies, Non-Cyanide Processes

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycling/Purification of Plating/Cleaning Baths

3. **Agency:** Navy

4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)

5. **Proposal ID:** #070

6. **Problem Statement:**

The goal of this effort is to develop innovative techniques for prolonging process bath life and for recycling hazardous materials from spent process baths to reduce the generation of hazardous wastes (HWs). DoD electroplating shops use process solutions containing hazardous materials for plating, metal stripping, acid etching, alkaline cleaning, anodizing, and other metal finishing operations. The effective life of these solutions is limited by the increasing levels of contaminants that are dragged in from the parts being plated or cleaned. These contaminants reduce plating and cleaning efficiency and will eventually adversely affect the quality of the metal finishing operation. As a result of this contamination, the "spent" bath must be periodically dumped. Large volumes of concentrated HWs are generated from these process solutions that become spent due to buildup of contaminants.

Based on Navy data collected for CY-90, the largest volumes of spent process baths in decreasing order included sodium hydroxide, chromic acid/sodium dichromate, hydrochloric acid, cyanides, sulfuric acid, nitric acid, electroless nickel and nickel sulfamate. While ongoing RDT&E efforts to develop new technologies for eliminating chromium and cadmium (cyanide) plating operations will reduce the use of these particular process baths, many of the alternative processes will require purification of contaminants (i.e. replacement of chromic acid anodizing with sulfuric-boric acid anodizing, replacement of cadmium plating with zinc-nickel plating, use of electroless nickel coatings in place of hard chromium plating). Development of alternative application techniques such as spray casting which eliminate the use of chemical process solutions are in the developmental stages and not currently available. Cleaning and stripping solutions will continue to be used. In addition, many new aqueous cleaning solutions are being used to eliminate solvent cleaning with CFCs. These cleaning solutions will require purification to maximize the solution life.

Separation technologies such as ultrafiltration, carbon absorption, ion exchange, electrolysis, membrane electrolysis, electrodialysis, and diffusion dialysis will be investigated for use in removing contaminants from plating/metal cleaning process baths. This effort will address a variety of process solutions and removal of different contaminants that buildup. The process baths requiring purification will be prioritized based on DoD volumes of solution waste generated, disposal costs, toxicity, and continued use. The impact of ongoing RDT&E efforts to eliminate chromium and cadmium plating will be considered as well as anticipating requirements for purification of alternative process baths. Several technologies will be developed for specific applications as required. Test and evaluation of purification technologies with applicability to a variety of process baths will be given the most emphasis. Purification of alternative plating solutions will be considered in the test program.

This project is an ongoing SERDP effort. The Navy effort was enhanced under FY93 funding as a joint Navy/Air Force/EPA project. It addresses SERDP Thrust 3.A.3.a Pollution Prevention for Metal Working/Plating and Finishing. It supports the SERDP goal to minimize or eliminate hazardous wastes through improved in-process treatment technologies for key industrial operations, including metal preparations.

7. Project Description:

The objective of this effort is to develop effective methods and on-line systems for purification/rejuvenation of electroplating (chrome, nickel, electroless nickel, copper, etc), anodizing, and metal cleaning solutions (acids, alkalies). Data will be collected from DoD plating shops to identify the contaminant levels for major process baths and current bath maintenance practices. Contaminant buildup in alternative process baths under test demonstration will also be investigated. Separation technologies such as membrane electrolysis, electrodialysis, ion exchange, carbon absorption, and ultrafiltration will be investigated for removal of metal and/or organic contaminants from plating and cleaning solutions. Chemical/electrochemical destruction technologies for removal of residual organic contaminants will also be investigated. An assessment of technologies completed by the Navy in FY92 will be updated and expanded to identify the status and applicability of emerging technologies for purification/rejuvenation of Navy and Air Force process solutions.

Laboratory tests will be conducted as needed to evaluate alternative technologies. The most promising technologies will be identified for each major process solution disposed by Navy and Air Force plating operations. Field testing of selected technologies will be performed to determine the effectiveness and to optimize design and operational parameters for each purification system developed for specific process baths. Appropriate planning, design, operation, and maintenance criteria will be developed for technology transfer of each system to DoD plating operations and coordinated with American Electroplating and Surface Finishing (AESF) society for transfer to private industry. The technical risk of this effort is low. The project addresses the Tri-Service EQ Strategic Plan, Requirement I.3.b. Reuse/recycling of hazardous wastes generated from electroplating operations.

8. Expected Payoff:

Development and demonstration of bath purification technologies will provide in-process treatment of plating, acid etching, pickling, alkaline electrocleaning, chromating, anodizing, and other solutions. Hazardous wastes generated from these metal finishing processes could be reduced by 75% with the extension of process bath life. Navywide hazardous wastes could be reduced by 375,000 gal/yr providing a saving of $1.3M per year or more depending on the cost for disposal. In addition, cost savings for chemical replacement is estimated at $1.5 M/yr. DoD-wide savings would be at least tripled. The anticipated non-economic benefits include improved product quality of finished parts by reducing contamination in the plating/cleaning processes. Users include Navy and DoD plating shops as well as many potential users of this technology in the public and private sectors. As there are many thousand electroplating and surface finishing facilities in the US, there would be high interest and potential for transfer to industry.

9. Milestones:

1.	Collect DoD Plating Shop Data	01/94
2.	Complete review of advanced and emerging separation and organic destruction technologies.	03/94
3.	Identify technology alternatives for each major process bath and prepare updated technology assessment report	06/94
4.	Develop experimental design for laboratory and field evaluations to address technology/process bath matrix	06/94
5.	Conduct feasibility studies to assess the effectiveness and performance of alternative bath purification systems	03/95
6.	Prepare technology evaluation report	06/95
7.	Optimize designs of preferred systems	06/95
8.	Conduct onsite field testing and evaluation of selected technologies	03/96
9.	Develop Technology Transfer Package(s)	09/96

10. Transition Plan:

Documentation covering planning, design, operation, and maintenance of bath purification systems will be prepared for technology transfer to Navy and DoD activities. This technology transfer package will be published as a final deliverable. The technology transfer package will be provided to appropriate Navy, Army, and Air Force activities for implementation including Air Force's System Program Office and the Technology Transfer Division of Air Force's Center for Environmental Excellence. Private industry will have access to the information developed and, with it will be able to apply the technology as desired. In addition, the capabilities of EPA's Center for Environmental Research (CERI) will be used to provide technology transfer of information to private industry.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	600	800	800	2200

12. Performers:

The performers include the Naval Facilities Engineering Service Center with joint participation from Air Force's Wright Laboratory, Manufacturing Technology Division and EPA's Risk Reduction Engineering Laboratory. Wright Laboratory will assist in the collection of plating shop data, development of contracted efforts for pilot and field testing, and identification and coordination of field tests at selected Air Logistic Centers. RREL will assist in laboratory and bench scale studies of advanced membrane technologies that could be applied to process bath purification and in transfer of technology to private industry. The POCs for partners in this effort are Mr. Roger Wilmoth, RREL, Toxics Control Branch, (513)569-7509 and Mr. Dan Brewer, WL/MTX, (513)255-36701 x208.

13. Principal Investigator:

Ms. Jennie Koff, Code 421
Naval Facilities Engineering Service Center
560 Center Drive
Port Hueneme, CA 93043-5003
TEL: (805) 982-1674
FAX: (805) 982-1409

14. Keywords:

electroplating, metals removal, membrane separations, purification

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Extraction and Recycling of LOVA Propellants Using Supercritical Fluids

3. **Agency:** Army

4. **Laboratory:** U.S. Army Research Laboratory

5. **Proposal ID:** #660

6. **Problem Statement:**

Objective: Solid gun propellants are currently destroyed by open pit burning or incineration; supercritical fluid (SF) recycling, rather than destruction, would have both economic and environmental advantages. Unfortunately, the ingredients of composite LOVA (nitramine) propellants have insufficient solubility in non-reactive SFs (e.g., $C0_2$). The objective of this new program is to identify suitable SF solvents for use in extracting and recycling the ingredients of solid LOVA gun propellants being developed for AMC munitions development programs.

Background: Supercritical fluids (SFs) have two potential environmental-related applications related to energetic materials demilitarization: destruction via oxidation in SFs (HAZMAT destruction), and "solventless" SF extraction/separation for purposes of recycling (pollution prevention). The first area is being actively pursued (see C&E News, Dec. 23, 1991): the DoD has established a pilot plant that uses supercritical water to destroy military toxic wastes. For the long term, however, recycling should be the preferred approach. There is a fundamental dilemma, however. While the energetic material (RDX) and polymeric binder of LOVA propellants tend to be highly soluble in the (polar) SF solvents used for destructive oxidation (e.g., supercritical H_20, TC=374°C), the solubilities in "inert" solvents (e.g., supercritical $C0_2$, TC=31°C) that one would like to use for extraction/recycling are too low for the process to be economically feasible. (This is not a problem for double base propellants, since the energetic plasticizer nitroglycerine is soluble in SF $C0_2$, and therefore easily soluble from the nitrocellulose binder.)

7. **Project Description:**

The research involves experimental and theoretical investigations of the effectiveness of polar "modifiers" in increasing the solubility of energetic materials (e.g., HMX, RDX) in supercritical $C0_2$. The goal is the identification of polar "modifiers" that a) significantly increase solubility of the solid propellant components in SF $C0_2$, b) do not result in hydrolysis or other chemical degradation of the propellant ingredients, and c) can either themselves be recycled (SF extractors can operate closed-cycle), or are as close as possible to neat $C0_2$ in having negligible environmental impact. In addition to polar modifiers, several alternative (to $C0_2$) supercritical solvents have been identified and are being investigated; these are fluids with significant dipole moments, but that are not ozone-depleters.

For other systems/applications, $C0_2$ modifiers at the 1-5% level have increased solubilities by up to several hundred percent. This research is probing the relationship between modifier molecular structure and its effect on solubility of nitramine energetic materials and other

propellant ingredients. The research also involves finding the optimum SF conditions (e.g., temperature, pressure/density) for promising $C0_2$-polar modifier supercritical solvents.

The experimental work involves measurement of nitramine (and other ingredient) solubilities in supercritical solvents using a variety of polar modifiers, and under several supercritical conditions (e.g., both close to- and far from- the critical point). Two experimental techniques are being used to measure solubility. One involves spectroscopic detection using an optical (windowed) supercritical cell; the other involves use of a supercritical fluid extractor (SFE) interfaced to a supercritical fluid chromatograph (SFC). During FY93, the effect of a series of polar modifiers on the rate of RDX extraction from LOVA M43 propellant was investigated. For P = 5,000 to 10,000 psi and T from 31 to 50° C, enhancement factors of up to 120,000-fold have been measured, compared to neat $C0_2$. Dissolution rates and solubilities for several alternative SFs (primarily non-ozone-depleting fluorocarbons) were also measured during FY93.

The theoretical work serves to guide the experimental effort: theoretical solubility predictions are being used to identify promising solvent-modifier systems,2~3 with other theoretical techniques 4 5 being used to generate the complex "phase diagram" from a limited number of solubility measurements, thus increasing the number of modifiers that can be investigated in a reasonable amount of time. The theoretical solubility prediction techniques involve ab initio methods, as well the use of molecular modeling software (BioSym's Insight 11 operating on a Silicon Graphics workstation) for predicting solubilities. This is apparently the first application of these techniques for prediction of SF solubilities.

This project received FY92 and FY93 SERDP funding for implementation during FY93 and FY94.

8. Expected Payoff:

Prevention of pollution associated with disposal of Army (and Navy) gun propellants; associated reduction of life-cycle cost of munitions.

9. Milestones:

1.	Measured RDX solubilities in several alternative (unmodified) SF solvents	05/93
2.	Measure effectiveness of 10 polar modifiers (at 31-50°C, 5,000-10,000 psi) for extraction of RDX from LOVA propellant M43	09/93
3.	Evaluated molecular modeling techniques for solubility predictions	11/93
4.	Measure full phase diagrams (vs. density and T) for RDX in most promising polar modified $C0_2$ systems and alternative SF solvents	07/94
5.	Design and test (laboratory-scale) extraction/recycling schemes for M43 based on results from 6.1 program; determine if size reduction important/necessary	09/95
6.	Larger-scale experiments; explore & optimize M43 propellant extraction/recycling schemes; begin work on new (energetic binder) LOVA formulation	09/96
7.	Pilot-plant scale demo of most promising recycling scheme for M43	09/97
8.	Analysis of data from demonstration; final report	06/98

10. Transition Plan:

Progression is from 6.1 research into solubility relationships and modifiers (through FY94), then 6.2 research into extraction/recycling schemes beginning in FY95. If successful, technology transfer would take place via a pilot plant demonstration at a LOVA manufacturing site in

FY97; this would be a venture jointly funded with SERDP by PM-TMAS and/or the Naval Surface Warface Center, Indian Head (NSWC-IH), where LOVA gun propellant is currently manufactured.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	FY98
SERDP	400	450	550	400	350	100

12. Performers:

Most research (6.1, 6.2) is being carried out in-house, with technical interactions involving ARO contractors, Battelle Northwest, University of Delaware, University of Wisconsin, and University of Texas (Austin). During FY93 and FY94, there were small contracts for technical support and instrument development with the CECON Group (Wilmington, DE) and CCS Instrument Systems, Inc. (Avondale, PA). During FY95 (using FY94 SERDP funds), a somewhat larger technical support contract is anticipated, perhaps with Phasex Corp. (Lawrence, MA); they would then be involved in design and construction of the "scale-up" facility to be used in the technical demonstration in FY97. Joint sponsorship will be sought from PM-TMAS or the LOVA manufacturer (Navy/NSWC-IH) for the 6.3 portion of the program. Related Activities: This project is being closely coordinated with related projects at MRDEC (MICOM) and RMP (AP-based, and NC-based propellants, respectively). For example, discussions are under way with Bill Melvin of MRDEC so that cost and other comparisons can be made with the MRDEC liquid ammonia process once an optimum supercritical fluid solvent system (and optimum conditions) has been established.

13. Principal Investigator:

Dr. Jeffrey B. Morris
Weapons Technology Directorate Army Research Laboratory
AMSRL-WT-PC ARL
Aberdeen Proving Ground, MD 21005-5066
TEL: (410) 278-6148
DSN 298-6148
FAX: (410) 278-6150

14. Keywords:

Propellant, LOVA, Demil, Extraction, Recycling, Supercritical Fluid

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion

3. **Agency:** Army

4. **Laboratory:** Army Research Laboratory, Aberdeen Proving Ground, MD

5. **Proposal ID:** #680

6. **Problem Statement:**

Goal: To reduce production of waste and unnecessary energetics material in manufacturing for guns and rockets. To completely eliminate inventories of high explosives (RDX, HMX, PETN, TNT), pyrotechnics (blackpowder, lead styphnate, azides) and nitrocellulose-based igniter materials from the inventory of energetic materials used in propulsion through the use of laser radiation as the primary ignition source. To avoid pollution problems associated with the demilitarization/incineration of these materials. One laser can replace thousands of lbs of this material in the life cycle of a gun system.

Background: The chemical ignition materials used in gun propulsion consist of various high explosive, blackpowder, nitrocellulose-based propellants, benite, BKN03 and other pyrotechnics. Demilitarization of the vast inventories of these sensitive materials via incineration is dangerous and can produce pollutants, carcinogens and toxic agents. There are also safety considerations in the manufacture, handling, storage, disposal or recycling of these energetic materials which greatly impact cost. This proposal addresses a means to negate all of these concerns through the development of technology by which propellant ignition materials will be eliminated from DoD inventories. Rather then initiating research to understand or minimize the hazards associated with incineration, advanced laser technology will be utilized as a replacement for large caliber gun propulsion. Problems associated with the disposal of ignition materials will no longer exist when lasers are integrated as the primary gun ignition source.

7. **Project Description:**

Previous Efforts: The concept of the use of lasers as an ignition source for propulsion applications where the primary purpose is to eliminate stockpiles of energetic materials in order to completely avoid demilitarization and pollutant formation problems which arise through incineration has not been previously considered.

Technical Objective/Approach: Set up laboratory-scale experiments for propellant ignitions using our in-house state-of-the-art laser laboratory with full electro-optics diagnostics capability. Design laser-based ignition systems for propulsion using laser energy distributed through optical fibers. Perform parametric investigations of laser parameters such as wavelength, pulse width, repetition rate to optimize performance. Test ignition configuration is simulators. Transfer ignition technology to large caliber gun and rocket motor designers for integration into current and future systems. All chemical propellant ignition material will be eliminated from energetic materials inventories.

8. Expected Payoff:

Potential Users: DOE, DoD, ARDEC, MICOM, Benet, AFAS, Navy, NASA, Air Force, Industry will use technology to eliminate these dangerous and unnecessary materials from their inventories. Dual Use Technology developed such as laser systems, optical components, optical feedthroughs will benefit both military and civilian markets. Four ongoing SBIR programs to develop technology in place.

Impact: Removal of these materials from current inventories, eliminate environmental pollution, waste and hazard from disposal, immense cost savings from safety considerations in all aspects of manufacture, production waste in manufacturing, storage and handling, benefit to the soldier in the field from a safer and simpler weapons system (less vulnerable).

9. Milestones:

Lab Experiments, Range Tests and Data Analysis	FY96

10. Transition Plan:

Technology will be transferred to ARDEC and coordinated with Benet Labs through 6.3 program.

Relationship to DoD/DOE: To reduce production of waste and unnecessary energetic materials in manufacturing. This proposal seeks to eliminate pollution hazards from propellant materials demilitarization, incineration and recycling by eliminating their need in current applications.

Relationship to Ongoing Work: Participants: ARDEC, MICOM, Benet, PM-AFAS, Navy, China Lake, NASA, Air Force. The defense industry, international defense institutions (Germany, UK) and the US DoD community are utilizing lasers as a means of augmenting propulsion. This represents the first effort to design a propulsion system with the central purpose being the elimination of stockpiles of energetic materials to avoid pollution from demilitarization and incineration. Our preliminary work has demonstrated that the laser can achieve these goals.

11. Funding: ($K)

FY94	FY95	FY96	TOTAL
200	250	175	625

12. Performers:

This work will be performed at ARL. Demonstration testing will be done at ARDEC.

13. Principal Investigator:

Dr. Brad E. Forch, ARL
Phone: 410-278-7067 FAX: 410-278-6150

14. Keywords:

Laser, Ignition, Propulsion, Primer, Gun, Optical Fibers

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents

3. **Agency:** Army

4. **Laboratory:** Army Research Laboratory, Aberdeen Proving Ground (ARL-APG)

5. **Proposal ID:** #695

6. Problem Statement:

Waste solid gun propellants are destroyed primarily by open pit burning or incineration. Because of environmental concerns, the DoD has recently established a pilot plant to destroy military toxic wastes by oxidizing the solids in non-polluting polar reactive supercritical fluids (SFs) such as SF H_2O at T_c=374∞C. Extraction and subsequent recycling of the propellant, as opposed to destruction, using a non-polluting, inert SF solvent would have obvious economic and environmental advantages. The components of composite solid LOVA propellants (an energetic material [RDX] and polymeric binder) have very low solubilities in an inert sf solvent such as CO_2, making the extraction process economically infeasible. A proven method for enhancing the solubility of the propellant in SF CO_2 is addition of simple polar modifiers at levels as low as 1-5%. The solubilities have been shown to increase up to several hundred percent upon this small addition. The object of this research is to complement an experimental effort at the ARL to determine the optimal physical conditions and chemical makeup of an effective SF CO_2/modifier solvent using well-established computational chemistry techniques and high performance computers. Computer simulation is an inexpensive and safe method of filtering a wide assortment of chemical systems, leading the experimentalist more quickly to successful candidate solvents.

7. Project Description:

The research will be divided into two complementary parts that will be worked on in parallel. The first part will give insight into the actual dynamical event of the first step in the SF solvation process, the dissolution of an RDX crystal into SF solvent. The second part will be more rigorous quantum chemical study on the relative abilities of real modifiers to stabilize an RDX molecule in the SF solvent.

Part 1. The simulation model will consist of an RDX crystal immersed in SF CO_2 doped with model modifier molecules (MMs). The CO_2, MMs and the crystal will all be described by purely classical potential energy function that includes hydrogen bonding, dispersion forces, and electrostatic interactions. The description of the MMs will be flexible enough to span a wide range of both polarity and polarizability, since these characteristics often associated with dissolution capability of a solvent. Constant pressure, constant temperature rigid body molecular dynamics simulations will provide a dynamical picture of the molecular micro-environment of the system as it dissolves, as well as indicate relative ability of each different SF mixture to break up the lattice. This qualitative picture can lead to selection of modifiers with

specific chemical and physical properties that should maximize the dissolution of RDX in the SF solvent.

Parameters that will accurately describe the intermolecular interactions can be obtained through the use of recently developed quantum chemical techniques such as nonlocal density functional theory (NDFT)[2] and symmetry adapted perturbation theory (SAPT)[3,4]. The molecular structure of each compound will be determined once by doing geometry optimizations of each isolated molecule using NDFT. These molecular structures will then remain fixed. The intermolecular interactions will be fitted to pairwise interactions between the different compounds using the SAPT method developed specifically for this task. In addition, the intermolecular interaction terms will include the ability of the partial charges, and hence the multipole moments of each molecule, to adjust to the electric field around it as the molecular dynamics proceeds.

Part 2. This part of the modelling combines quantum and classical methods to produce a more quantative prediction of solubility by attempting to calculate the free energy of solvation, i.e., $\Delta F = \Delta H - T\Delta S$, for one or more RDX molecules in SF CO_2 as a function of the specific modifier molecules included in solution. The solution space will be divided into two zones; 1) an inner "action" zone, and 2) an outer "bath" zone. The action zone will consist of an RDX molecule, the first and second treated purely quantum chemically for the determination of changes in the enthalpy, ΔJ, using a combination of NDFT and SAPT. The action zone will be surrounded by the bath zone made of a layer of CO_2 molecules described by a classical potential for the quantum chemical action zone. Such a combined quantum/classical approach has already been used to study catalysis on zeolytes[5].

The total quantum chemical energy calculated for the action zone will give the enthalpy of the (RDX + SF CO_2 + MMs) solution. This will be calculated for each of the proposed modifier compounds. The change in enthalpy, ΔH, needed as part of the free energy, can then be obtained by a thermodynamic calculation and the sum of the enthalpies from each isolated molecules will be approximated by calculating the full vibrational spectrum of the action zone. The ΔS will be calculated as the difference between the sums of the vibrational energies over the action zone first with the modifier molecules included, then excluding the modifier molecules. This difference in total vibrational energies should give the contribution of the MMs to ΔS for solvation of RDX in the SF mixture.

1. J.M. Dobbs, J.M. Wong, R.J. Lahiere and K.P. Jonhston, *Modification of supercritical Fluid Phase Behavior Using Polar Cosolvents,* Ind. Eng. Chem. Res. 26, 56 (1987).

2. R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules,* Oxford University Press, NY 1989

3. T. Cwiok, B. Jexiorski, W. Kolos, R. Moszynski, and K. Szalewicz, J. Chem Phys. 97, 7555 (1992), and references therein.

4. B. Jexiorski, R. Moszynski, A. Ratkiewicz, S. Rybak, K. Scalewicz, and H.L. Williams, in: *Modern Techniques in Computational Chemistry: MOTECC-93,* ed. E. Clementi, in press.

5. J. Sauer, *The Combined AB Initio and Classical Potential Approach to Zeolite Catalysis,* Presented at BIOSYM, Catalysis and Sorption Consortium Meeting, Parsippany, NJ, October 7, 1993

8. Expected Payoff:

Timely development of a method for recycling solid propellants to keep the Army in compliance with EPA standards for reducing atmospheric, ground, and water pollutants. Computer modelling has been widely recognized by the chemical and pharmaceutical industries as cost cutting technique in the pursuit of chemical properties for systems of interest to the manufacturer (see; "Promise of Rich Payoffs Drives Computer-Aided Chemistry" in *Research & Development Magazine*, p. 28, September 1993; and "The Question Is Not Whether But When To Go For Computer Aids", in *Today's chemist At Work*, vol. 2, p. 20, 1993). The same cost cutting needs are obvious in today's environment of shrinking DoD budgets. Furthermore, computer modelling will reduce both the personal and environmental risks associated with experiments involving military hazardous materials.

9. Milestones:

1.	Procure and configure theoretical chemistry computer software	11/94
2.	Complete initial development of Solid RDX computer model and	3/95
3.	Complete development of action and bath zones	9/95
4.	Molecular dynamics simulation of SF system -- ranking of modifier properties	
5.	Predict free energies of RDX in SF/MM solvents	9/96
6.	Continued predictions of free energies and consider possible alternative SFs	9/97

10. Transition Plan:

Once the theoretical chemistry models are in place and verified, calculations on various model modifier/CO_2 SF solvents will begin. These calculations will give a microscopic description of the physical state of the system at the various stages of the solvation process. The results of these simulations will rank the modifiers according to their ability to increase the solubility of solid propellants in SF CO_2 and possible other supercritical fluids. This information will build a data base useful by experimentalists in selecting new modifiers and supercritical fluids.

11. Funding: ($K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	350	350	350	350	1400

12. Performers:

Dr. George Adams, Army/US Army Research Laboratory, APG, MD; Professor Krzyatof' Szalewic, Depts of Chemistry and Physics, University of Delaware - Assist in studies of intermolecular interaction energies using his SAPT methods; Professor Donald L. Thompson Department of Chemistry, Oklahoma State University - Assist in the classical molecular dynamics simulations.

Coordinated with the POC for the experimental research - Dr. Jeffrey Morris, Army/US Army Research Laboratory, APG, Md.

13. Principal Investigators:

Dr. Betsy Rice
US Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005-5066
Phone: 410-278-6183
FAX: 410-278-6150

Dr. Cary Chabalowski
US Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005-5066
Phone: 410-278-6094
FAX: 410-278-6150

14. Keywords:

Supercritical Fluid Extraction, Propellant Recycling; solid Propellant Extraction

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** DoD/DOE Clean Agile Manufacturing of Energetics

3. **Agency:** Navy

4. **Laboratory:** Office of Naval Research (ONR)

5. **Proposal ID:** #063

6. **Problem Statement:**

Approximately 100 million pounds of energetic materials (propellants, explosives, and pyrotechnics (PEP)) are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/ illuminators. Many are based on energetic materials that could negatively impact the environment during an item's life cycle.

Under Executive Order 12856, Federal facilities are required to achieve a 50% reduction of hazardous wastes by 1999. PEP chemicals and products are produced in government operated, GOCO, and defense contractor facilities. Ever stricter environmental regulations and waste restrictions are curtailing production of some PEP chemicals (for instance TNT). Department of Energy and NASA also have PEP waste reduction requirements.

Past waste reduction has been accomplished by cleaning up individual PEP production processes. Future waste reduction can be achieved by pollution prevention measures throughout the PEP product life-cycle. The product life-cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim and recycle or reuse excess material.

In his Earth Day speech last April and his recent Executive Orders, President Clinton demonstrated that the Government should lead by example and that Federal facilities should become the leader in applying pollution prevention to policies and daily operations. Similarly DoD has raised "environment" to the Deputy Under Secretary level, has re-emphasized life-cycle environmental and cost considerations early in the acquisition cycle, and has stressed partnerships with industry and the R&D community in this area. Additionally, there are significant parallel efforts by different groups outside the Government that share common goals and objectives in life-cycle assessment (LCA) and in modeling and simulation of industrial processes.

This SERDP program is a continuation of a five year, technology demonstration initiated by the Office of the Director, Defense Research and Engineering and endorsed by the SERDP Scientific Advisory Board in January, 1993. The first year funding ($2M FY93) was received in November, 1993. $3.7M is requested for FY94.

7. Project Description:

7.1 Technical Objective: The objective of this program is to develop integrated product/process development (IPPD) technologies and tools to achieve concepts for reconfiguring existing PEP life-cycle facilities into a clean, agile enterprise that will function economically with total life-cycle wastes reduced by 90%. In the context of this proposal, life-cycle facilities are defined to be the set of existing, geographically separate, PEP facilities that design, develop or produce PEP products, recycle the production by-products into usable products, or recycle PEP parts returned as excess from the ordnance inventory. Many facilities operate under the oversight of the Army Single Manager for Conventional Ammunition.

Significant advances have been made synthesizing new PEP chemicals (e.g., ADN, CL-20, NTO, TNAZ). These new chemicals could enable significantly lower pollution PEP products. Since processes or facilities that produce and handle these new materials have not yet been specified, designed or built, they are prime candidates for demonstration of the IPPD approach that will enable design of the clean, agile facilities that will be able to comply with future environmental regulations.

The Environmental Protection Agency (EPA) has established a Life-Cycle Assessment guideline to evaluate environmental effects consistent with criteria established by the Society for Environmental Toxicology and Chemistry (SETAC). This EPA guideline, including Peer Review, Panel, will be followed to identify phases of the PEP life cycle where considerable pollution is generated. Simulations coupled with the life-cycle assessment can be used to test alternative routes for preventing pollution.

7.2 Technical Approach: Government and industry PEP R&D labs, pilot plants, and production facilities will be organized into a program network. Models and simulations will predict life-cycle pollution. Pollution prevention technologies and new facility concepts will be experimentally tested in existing facilities available to members of the program network. When use of existing facilities is not practical, a special demonstration testbed may be built. Facility design concepts will be developed, addressing chemical engineering unit operations, mass/energy balances, regulatory requirements, safety, pollution prevention and costs.

7.2.1 Life-Cycle Assessment Simulation Tool: A Process Modeling System enterprise simulation framework will be used to organize the PEP environmental life-cycle assessment following EPA guidelines. For example, this project might exploit the G2 simulation tool used in a Technology Reinvestment Project (TRP0. The simulation will test a variety of facility concepts. It will also be used to assess the complete pollution picture for the PEP product life-cycle. Models and simulations will be validated by existing data and experiments done throughout the program network.

7.2.2 New Materials and Processes to Prevent Pollution: The synthesis practice is well understood for various new energetic ingredients such as: ammonium dinitramide (ADN), hexanitrohexaazaisowurtzitane (CL-20), nitrotriazolone (NTO), energetic polymers with polyether backbones (glycidyl and oxetane backbones), and energetic plasticizers for formulation into advanced energetic formulations. Energetic monomer and polymer scale-up in continuous flow reactors have been initiated at Thiokol and Aerojet. Synthesis of ADN in laboratory and small pilot facilities is being supported by SDIO, NASA, MICOM and ONR at SRI International, NSWC-IH and Thiokol. An alternate synthesis approach for HMX production was developed by the Army and Lawrence Livermore National Laboratory in the MUSALL project. These new

materials and synthesis methods make practical a search for production methods that reduce pollution through the PEP life-cycle.

Reclamation of PEP formulations can be done using solvents in the super critical state. ADN offers an unusual reclamation opportunity. ADN is a chlorine free oxidizer which could replace ammonium perchlorate, eliminating the ozone depletion and acid rain Space Shuttle launch issues. ADN decomposes to ammonium nitrate and N_2O (laughing gas) in an acidic aqueous environment. This property makes possible the conversion of future ADN based PEP into ammonium nitrate for use as a commercial fertilizer.

Program demonstrations will include a solventless or reduced solvent technique in place of conventional solvents to process PEP and supercritical fluid extraction techniques to reclaim and reuse PEP returned from the arsenal.

The Army Production Base Modernization Activity (of the Army Single Manager) supports development of improved production capability at GOCO facilities. They have a demonstration testbed in the design stage, called the Flexible Manufacturing Facility for Energetic Materials, which could be adopted for the mixing, processing and loading phase of this effort.

7.2.3 Demonstration of Critical Pollution Prevention Technologies by the Program Network: Various processes and products will be evaluated in a test program utilizing laboratories and pilot plants in an experimental network. These experiments will demonstrate new PEP chemicals, products, and processes that are practical for safe, cost effective, environmentally clean implementation during the PEP life-cycle, and satisfy ordnance performance requirements.

7.3 Relationship to the DoD/DOE Environmental Objectives: This effort directly supports Pillar 3 (Pollution Prevention) of the Tri-Service Users Requirements, Items I.6.a-f and I.6.h: Reduction of hazardous waste by 50% in ordnance manufacture. The reconfigured processing of new PEP chemicals should produce significantly less waste than the Pillar 3 objective. It also supports accomplishment of Pillar 3 Item III.2.d-f: Methods for developing environmentally sound weapons systems. This effort also supports the DOE Defense Programs Waste Minimization/Pollution Prevention Program (DOE Order 5400.1) strategy.

8. Expected Payoff:

This program will result in new PEP materials, processes and concepts for reconfiguring existing PEP facilities to reduce hazardous wastes by a factor of ten, almost twice the 1999 national goal for pollution prevention. The output of this program is intended to mitigate price increases for future PEP products due to cost of complying with environmental regulations. Satisfying regulations will help curtail facility shutdowns or unscheduled retirement of ordnance systems.

Utilizing the program network of existing laboratories, pilot plants, and production facilities will:

1. Preclude duplication of existing facilities;
2. Reduce construction funds needed for new plants; and
3. Allow each unit to contribute to the life-cycle phase in which it is most knowledgeable.

At the end of the program, a PEP life-cycle simulation tool will be available to the Army Single Manager to assist in reducing life-cycle pollution as the PEP production base continues to be modernized. The models and simulations will provide an understanding of current operations,

assist in evaluating alternative processes to surpass the national goal, and quantify future environmental gains which might be achieved through clean and agile facility design.

In addition, this program will provide the basis for evaluation of the potential for using the modeling tools for commercial/dual-use applications (e.g., energetic polymers and anti-fouling coatings for ships produced using the same facilities; reusing PEP in commercial blasting products).

9. Milestones:

FY93 SERDP funds available since November, 1993 are being used as follows:

1. Technology transition plan and program network established	6 MO
2. Pollution prevention product/process surveys complete	9 MO
3. Life-cycle simulations of two RDX products (PBX N109 in GBU-24 bomb and M43 propellant in the M-900 cartridge for a tank round)	12 MO

FY94 SERDP funds now requested will be used to:

1. Initial pollution prevention technology prioritization	15 MO
2. Complete initial EPA Life-Cycle Assessment	18 MO
3. Select and develop/apply priority PEP materials and processes, e.g:	24 MO
4. Clean crystalline explosives, polymers, plasticizers, oxidizers and binders Clean life-cycle, high performance propellant Supercritical processing to avoid solvents Reuse/recycle of energetics Life-cycle simulation of clean, agile operation of pilot plants	24 MO

To be achieved with FY95-97 SERDP funds:

1. Simulation and experimental validation of reduction of	30 MO
2. Pollution for selected PEP products and new materials and processes Life-cycle trade-off analysis complete for selected products and new materials and processes	36 MO
3. Demonstration of the program network of life-cycle pollution prevention, product safety and performance for selected products	36 MO
4. Estimate life-cycle waste reduction relative to 1992 baseline	60 MO
5. Dual-use life-cycle assessment simulation tools for Army Single Manager	60 MO

10. Transition Plan:

The beneficiaries of this program are existing development, production and reclamation facilities operated for the Army Single Manager and DOE, GOCOs and commercial industry. Introduction of the new PEP chemicals and processes into the existing facilities will achieve the Pillar 3 ordnance DoD/DOE environmental objectives.

The Defense Conversion Armament Retooling and Manufacturing Support Program (ARMS), the NASA propellants production programs, and the DOE's complex reconfiguration program are potential customers.

The life-cycle modeling and simulation software will be transferred to the Army Single Manger, DOE, and GOCOs as well as commercial industries through the Cooperative Research and Development Agreements (CRADA).

Standards to support modeling and simulation will be integrated with industry standardization processes.

11. Funding: ($K)

FY93	FY94	FY95	FY96	FY97	TOTAL
2000	3700	5000	5000	3000	18700

12. Performers:

This program will be jointly managed by DoD and DOE. The Program Manager resides at the Office of Naval Research. A program advisory panel of government and industry PEP R&D and production managers will be formed. The panel will provide guidance to the program so as to ensure that the program products will transition into the DoD and commercial PEP production bases. The performers in the program network will include DoD ordnance laboratories (e.g., Naval Surface Warfare Center, Naval Air Warfare Center/Weapons Directorate, Army Research Development Engineering Center, Production Base Modernization Activity, Wright Laboratory Armaments Directorate), DOE National Laboratories (Los Alamos, Lawrence Livermore, Sandia), Army owned GOCO plants (e.g., Holston, Milan, McAlester), industry R&D labs (e.g., Thiokol, Aerojet), not for profit research institutes (e.g., Battelle Columbus), university consortia (e.g., Environmental Risk Reduction Center situated at the New Jersey Institute of Technology), universities (e.g., University of North Carolina), and small businesses (e.g., GENSYM). A peer review panel as described in the EPA Life-Cycle Assessment procedure will provide objective oversight.

13. Principal Investigator:

Dr. Richard S. Miller
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
TEL: (703) 696-4404
FAX: (703) 696-5383
e-mail: MILLER@onr-hq.navy.mil

14. Keywords:

propellants, explosives, pyrotechnics, environmental life-cycle assessment, pollution prevention.

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Solventless Pyrotechnic Manufacturing

3. **Agency:** Navy

4. **Laboratory:** Naval Surface Warfare Center, Crane Division (NSWC, Crane)

5. **Proposal ID:** #757

6. **Problem Statement:**

Because of the manufacturing use of volatile organic compounds (VOC)'s as processing solvents is a major source of the nation's pollutant waste streams, it is important to modify or replace processes in order to minimize or eliminate the use of VOC's. In our work we will focus on processes for manufacturing energetic materials that are concerned with pyrotechnic materials that are used, for example, as grain materials for air-countermeasures (infra-red decoys) and as igniters in Jet Assisted Take Off (JATO) and tactical rocket motors. These devices play major roles in certain defense areas, infra-red decoys being critical in the countermeasures suites deployed on tactical aircraft, while tactical rocket motors find important air defense and air-to-air interception applications.

The majority of these pyrotechnic compositions are currently manufactured using a crash precipitation method called the "shock-gel" process. The process generates large amounts of hazardous waste and constantly releases VOC's and toxic air pollutants (TAP's) to the environment. In the case of magnesium-Teflon-Viton (MTV), one such pyrotechnic used for solid rocket igniters, 1 lb of material generates from 0.3 to 1.5 gallons of waste solvent, depending on the processing facility.

Increasingly stringent environmental legislation, such as, the Clean Air Act Amendments of 1990, are increasing the manufacturing costs of these critical pyrotechnics by forcing the producers to reduce the hazardous air emissions and minimize the waste generated. Pollution abatement techniques alone will not be adequate to satisfy those restrictions. The obvious solution is to eliminate the solvents from the production process.

The FY94 Solventless Pyrotechnic Manufacturing project is aimed at eliminating all the hazardous solvents and associated emissions from current and future pyrotechnic formulations used in these critical applications. This 6.2/6.3 research will be performed concurrently at two separate divisions of the Naval Surface Warfare Center. Each division has unique expertise, facilities and equipment which will ensure success of the project.

The program is a combination of two separate efforts and as such would be composed of two phases. The first phase of the program would demonstrate a solventless cryogenic production process for the manufacture of MTV. This phase of the project would be a continuation of last years SERDP under the same title which dealt solely with cryogenic processing of MTV and the installation of a pilot scale facility at the Indian Head Division. The second phase would develop castable pyrotechnic formulations based on modern polymeric binder systems. This phase of the project would be a follow on the previously funded work and would be directed

toward the modification of a decoy composition now under development and toward appropriately modifying the in-service composition to make it castable. Currently the developmental work being conducted at the Crane Division is funded under a NAVAIR air-countermeasures PIP program and on ONR Electronic Warfare (Infrared Countermeasures) 6.2 research program.

Both phases of the proposed FY94 SERDP are complemented by similar efforts from U.S. Army Armament Research, Development and Engineering Center (ARDEC). In the cryogenic phase ARDEC is investigating the cryogenic processing of magnesium-Teflon-Hytemp (MTH) pyrotechnics. A joint effort in 1989 between the Indian Head Division and ARDEC resulted in two separate areas of investigation each focused on resolving the unique processing difficulties of each binder system. in the castable pyrotechnic phase ARDEC is developing a modification of the decoy composition as part of an ARMY AIRCMM project.

7. Project Description:

The objective of the Solventless Pyrotechnic Manufacturing project is to demonstrate two alternative approaches as methods of eliminating the hazardous waste and VOC emissions caused by the solvents used in the manufacture of MTV and similar pyrotechnic materials. Both the phase 1 cryogenic approach and the phase 2 castable pyrotechnic approach offer unique solutions to the pollution problems associated with the current solvent manufacturing process. Once both phases are completed they will provide the Navy and other DoD facilities with a full spectrum method to eliminate solvents and prevent VOC emissions from inservice and future pyrotechnic formulations. The project is listed under heading 3C5 of the Tri-Service Environmental R&D Strategic Plan (Green Book).

The cryogenic process for manufacturing MTV is a solventless process that has been demonstrated on a small scale. In the cryogenic process the Viton is cryogenically ground to a fine particle size using inert liquid nitrogen (LIN), Magnesium and Teflon are then chilled to LIN temperatures, Once the ingredients have reached equilibrium, they are mixed in a slurry of ground Viton and LIN. When a uniform distribution of the ingredients has been attained the temperature of the slurry is increased and the LIN is vaporized. Once the LIN has vaporized, the relatively free flowing pyrotechnic powder can be pressed or extruded into the appropriate size and shape using conventional molding technology. In terms of environmental liabilities, there are none. Nitrogen is an environmentally benign gas that makes up 79% of the air we breathe every day. Upon completion of Phase 1, the Navy will have a pilot plant capable of manufacturing solventless MTV and investigating other pyrotechnic applications.

The technical approach to demonstrate the solventless manufacture of pyrotechnics on a production scale is to (1) develop material handling techniques necessary to process the extremely cold material in a moisture free state, (2) install a pilot scale cryogenic MTV processing facility and (3) apply the cryogenic approach to other energetic materials manufactured by the solvent process.

The second phase of this project will use modern polymeric binder materials to formulate pyrotechnic compositions emphasizing their use for castable grains for decoy devices. Rocket composition formulating has driven the development of curable polymeric materials for application in energetic composites. We propose to formulate candidate pyrotechnic flare materials that employ binders of this type. The major technical challenge will be to find binder material that will cure to give pyrotechnic grains that perform in their decoy function as

required. We feel that there is great potential for application in developmental composition system of binder material candidates from the general class of azide-containing, curable pre-polymers. These binder materials are currently available in limited commercial quantities from al least tow manufactures.

For the standard, in service composition, the curable binder material must have a high content of fluorine atoms. Significant U.S. Navy funding for the development of one such material at Aerojet/Gencorp (Sacramento, CA) comes from ONR 6.1 programs, MIMI and MEQ. Potential non-military coatings applications will make the future availability of these materials less vulnerable to cuts in defense spending. Aerojet material can be obtained immediately for initial testing, but it is probable that Aerojet and/or other industry involvement will be contracted to develop materials tailored for our application.

Major tasks to be carried out in phase 2 include material procurement, laboratory scale formulating, functional testing, scale-up and performance testing. Some of the laboratory scale formulating and functional testing has already begun. Most performance testing will be carried out at the Crane Division using facilities and equipment elaborated specifically for the ground-based testing needed in their decoy development.

8. Expected Payoff:

Solventless pyrotechnic manufacturing will result in an environmentally compliant process which is safer and less costly than the current solvent manufacturing process. Both the cryogenic and the castable pyrotechnic processing approaches can eliminate the large quantities of hazardous solvent waste and VOC emissions currently generated in production. The elimination of waste streams from any process eliminates the need to install expensive solvent recover and recycling systems which will require additional energy usage, constant maintenance and possible upgrades to remain in compliance as regulators lower discharge thresholds.

The potential payoff in terms of hazardous waste elimination can be readily estimated from procurement figures for FY95. The Navy is planning on procuring some 100,000 lbs of flare decoy composition, the Army about half that and the Air Force approximately 5 times that of the Navy, totalling 650,000 lbs per year. This estimate only represents one family of decoy compositions, however, this amount of material will generate anywhere from 195,000 to 975,000 gallons of hazardous waste solvent. The current cost of disposing of waste solvent at the Indian Head Division is 600 dollars per 55 gallon drum. Based on this figure the total cost savings from the solvent elimination alone is anywhere from 2.1 to 10.6 million dollars. When everything is considered such as procurement costs of alternative materials these numbers are probably high. Based on the cryogenic approach, the Army has estimated a potential cost saving of $900,000.00 if their current 600,000 lbs per year "shock-gel" production process for flare decoys were replaced with the cryogenic process. The cost savings realized form not installing solvent reclamation and recovery systems have not been included.

Additional benefits may be realized in the area of product improvement. The use of curable polymers will give castable, curable compositions. Casting compositions into molds has the potential advantage over pressing grains from solids that it is easier to fabricate grains with complex shapes.

9. Milestones:

1. Select poly(oxetane) systems for trails	6/94
2. Procure flourinated materials	6/94
3. Evaluate ingredient precoolers and feeders	12/94
4. Procure ingredient precoolers and feeders	2/95
5. Procure large scale cryogenic mixing vessel	3/95
6. Install cryogenic equipment in MTV processing facility	5/95
7. Complete Lab-scale work	6/95
8. Select castable decoy system for scale-up	6/95
9. Debug and start up cryogenic equipment	6/95
10. Demonstrate cryogenic technology on a production scale.	8/95
11. Prepare final report, phase 1.	9/95
12. Complete preparation of 1-10 lb batches of materials for full size grain testing	6/96
13. Complete ground-based performance testing and select systems for further development	8/97
14. Complete final report, phase 2	9/97

10. Transition Plan:

The transition plan for first phase transition of the project cryogenic process expected to occur at the end of FY95 and the second phase will deal with the transition of the castable pyrotechnic technology. We expect that the Indian Head Division will convert their MTV igniter production to the new process having proofed the technology in MK 22 igniter systems. Their low production requirement will enable the Navy to use the equipment as a test bed to investigate other applications for cryogenic pyrotechnic manufacture. Transition of the second phase to advanced development will take place concurrently with flight testing or after initial flight testing of the candidate decoy device and occur at the Crane Division. The funding for this transition is expected to come from a product improvement program for a particular (in-service) decoy device. It is hoped that new pyrotechnic materials developed in this phase of the project may well be selected as candidates for the Air Forces Advanced Strategic and Tactical Expendables (ASTE) program and/or the Navy's Advanced Technology Expendables and Dispenser System (ATEDS) program both of which are seeking to improve the current in service decoy device configurations.

11. Funding: ($K)

	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	355	500	250	250	200	1555
NAVY	155	0	270	200	250	250	1125
TOTAL	155	355	770	450	500	450	2680

12. Performers:

The major performer for the castable pyrotechnic (phase 2) approach as well as the SERDP program management is the Naval Surface Warfare Center Crane Division. The cryogenic (phase 1) process development work will be performed by the Naval Surface Warfare Center Indian Head Division. We plan cooperative development of advanced fluorinated binder systems through contacts with industry.

13. Principal Investigator:

Dr. Norris J. Caldwell
Code 4073, Bldg. 2540
Naval Surface Warfare Center Crane Division
300 Highway 361, Crane, IN 47522-5001
Phone: (812) 854-2815
FAX: (812) 854-1711

14. Keywords:

Pyrotechnics, Flares, Binders, Hazardous Waste minimization, Solventless manufacture

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives

3. **Agency:** Army

4. **Laboratory:** Army Research Laboratory

5. **Proposal ID:** #682

6. Problem Statement:

The presently used Halons 1301 and 1211 fire extinguishing agents are being phased out due to their role in the catalytic destruction of the stratospheric ozone layer. There is presently a major effort underway within the DoD to find environmentally acceptable Halon replacement compounds. The goal of this research project is to develop a detailed flame chemistry computer model which will be able to predict the relative flame extinguishment properties of new Halon alternative compounds as well as to identify the possible formation of toxic flame products resulting from the use of the agent. This model, once fully verified and tested, will become a very important predictive tool for the RDT&E organizations for screening new compounds, or mixtures of compounds, and for interpreting results of full-scale testing.

This project is primarily a 6.2 effort since it builds upon a large body of basic research in combustion science. It will transition into 6.3a as the model is simplified to include only the important overall reactions. Ultimately, this reduced/simplified flame chemistry model is expected to be run on advanced PCs, rather than on the workstations which are presently required for running the full chemistry.

7. Project Description:

This project is a continuation of a project that was funded under SERDP Phase II during FY93, and which will continue to be funded under FY93 SERDP during FY94. The full year's of research funding in FY93 has yielded many results thus far. We have already obtained a set of flame structure profiles for methane/oxygen flames doped with various hydrofluorocarbon (HFC) compounds as well as Halon 1301. A flame model has been developed at NIST (largely with AF funding) for fluorine-containing inhibitor compounds which includes over 700 reactions.

Our basic approach involves a tightly coordinated research program of flame model development coupled with experimental verification. The flame experiments involve the use of a low pressure burner apparatus which contains a premixed laminar flow flame. The different flame zones are spread out at low pressure so that spatially-resolved profiles of the temperature and major/minor species can be made. We use two diagnostic techniques for the flame profile studies. These include the Molecular Beam/Mass Spectrometric (MB/MS) sampling as well as the Tunable Diode Laser (TDL) absorption techniques. Each of these methods has its inherent advantages and disadvantages. The detailed chemical flame mechanisms are tested on the basis of agreement with the experimental results. The modeling work typically involves many hundreds of elementary chemical reactions as well as nearly 100 flame species. Due to the

magnitude of the required computation, this work is typically performed on workstations or larger computers. However, after the complete reaction set is verified, then the number of reactions can be significantly reduced through the use of sensitivity analysis. The detailed kinetic models are based on accurate knowledge of thermodynamic and kinetic properties of the relevant species and reactions. For those reactions where previous data does not exist, an estimate has to be determined through the use of computational chemistry tools such as the BAC- MP4 and Transition State Theory programs.

After completion of the initial stage of model development and verification with the laboratory low pressure burner experiments, we will proceed to modify the models so that they can mimic, and ultimately predict, the large-scale fire extinguishment tests as carried out by TARDEC, NRL, and Wright-Pat. Also, we will adapt and test the models for the scenario where a combination/mixture of agents may be used. Our major goal is to develop such a high degree of confidence in the detailed chemistry models so that we can move to the next logical step, which is the reduction of the size of the model to include only the important reactions. This model simplification step will allow for (a) the models to run much more rapidly on the present workstations and (b) the models to be run on advanced PCs. Thus, these models will become much more readily available, and more generally useful, to the survivability engineers. We should reemphasize our position that we will continue to be very closely coordinated with the survivability organizations throughout this project, something that we believe will be very important in this urgent and rapidly developing Halon replacement program. Strat Plan Area: 3.H Fire Fighting Agents

8. Expected Payoff:

The successful execution of this research program will benefit all organizations concerned with survivability of military platforms involved in a fire scenario. The DoD organizations working in this area include TARDEC, ATCOM, Wright-Pat, and NRL. A flame chemistry model that includes fluorine, bromine, as well as iodine chemistry will be particularly useful as a screening tool for a wide range of candidate fire extinguishing agents. The ultimate development of the reduced chemistry flame model which can predict fire extinguishment behavior for mixtures of agents as well as the possible formation of toxic products, and which can be run on an advanced PC, will be a powerful tool for the survivability engineers.

9. Milestones: (Assuming FY93 SERDP funds are released Nov 93)

1.	Experimental decomposition kinetics for iodine and fluorine compounds, work performed at NIST	05/94
2.	Kinetic data base development to include iodine and bromine reactions, work performed at NIST	07/94
3.	Thermochemical calculations to estimate rate constants for key iodine reactions, work performed at NIST	07/94
4.	Experimental flame structure studies and modeling performed at ARL	09/94
5.	Expand model development to predict results of large-scale testing	09/95
6.	Develop and test models for mixtures of agents	09/96
7.	Develop reduced chemistry models to be run on advanced PCs	09/96
8.	Finish transfer of models for further use at survivability organizations	09/97

10. Transition Plan:

This research will continue to be closely coordinated with the survivability organizations (TARDEC, Wright-Pat, NRL) and the work will be coupled with these organizations as we develop models to predict large-scale testing of individual as well as mixtures of agents. Ultimately, once the reduced chemistry models are successfully developed so they can be run on advanced PCs, then these models will be transferred to the survivability organizations for more extensive use.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	300	400	450	400	250	1.8M

12. Performers:

This project will be performed at both the Army Research Laboratory and the National Institute of Standards and Technology. The work at both ARL and NIST will concentrate on extinguishment model development and verification and will be closely coupled with the larger-scale fire extinguishment tests conducted by TARDEC and Wright-Pat.

13. Principal Investigators:

Dr. Andrzej W. Miziolek
Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005-5066
TEL: (410) 278-6157 DSN: 298-6157
FAX: (410) 278-6150 e-mail: miziolek@brl.mil

Drs. Wing Tsang, Donald Burgess, and Michael R. Zachariah (Partners)
Chemical Kinetics and Thermodynamics Division
National Institute of Standards and Technology
Gaithersburg, MD 20899
TEL: (301) 975-2507 FAX: (301) 926-4513

Mr. Steve McCormick (Partner)
TARDEC
Survivability Technology Center
Warren, MI 48397-5000
TEL: (313) 574-5948 FAX: (313) 574-6674

Mr. Mike Bennett (Partner)
Wright Laboratory - U.S. Air Force
WL/FIVS, Bldg G3
1901 10th Street
Wright-Patterson AFB, OH 45433-7605
TEL: (513) 255-6302 FAX: (513) 255-2237

Dr. Ronald S. Sheinson (Partner)
Naval Research Laboratory
Code 6180
Naval Technology Center for Safety and Survivability
Washington, DC 20375-5342
TEL: (202) 404-8101 FAX: (202) 767-1716

14. Keywords:

Halons, Fire Extinguishment, Flame Modeling, Chemical Mechanisms, Vehicle Survivability, Flame Research

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Chemistry of Halon Substitutes

3. **Agency:** Army

4. **Laboratory:** Research Laboratory, Weapons Technology Directorate

5. **Proposal ID:** #666

6. Problem Statement:

Goal: Identify the potential halon replacement agents which are efficient in extinguishing fuel fires without producing excessive amounts of toxic by-products. The cost, space and weight claims of agents will be considered in assessing efficiency.

Background: While Halon 1301 has been universally accepted as a non-toxic fire extinguishing agent, certain toxic acids (HF and HBr) are produced when Halon 1301 is used to extinguish flames. The amounts of these acids are generally low enough to be considered merely a nuisance. However, in studies that the Army has conducted using Halon 1301 to extinguish crew compartment fires (mist fireball explosions) the acids have been analyzed in higher than acceptable concentrations. Potential halon replacements may well be less chemically effective than the halons. It is possible that even higher quantities of toxic gases may be produced from these materials than are produced from the halons. This information should be available before expensive full scale vehicle tests are conducted.

7. Project Description:

Previous Efforts: Private industry has initiated a program to identify acceptable substitutes for the halons. Industry's criteria of acceptability is somewhat different than the Army's. The severe space and weight constraints found in fielded combat vehicles, as well as the mist fireball explosion scenario are Army problems not addressed by industry. Likewise, the Air Force projects to find halon replacements for engine necell fires does not have the toxic gas production limitation that Army crew compartment fires have. The Navy is addressing the occupied volume fire problem, but not the mist fireball explosion problems.

Technical Objective: Identification of fire extinguishing agents which will be useful in controlling fires in Army combat vehicles. These agents must be non-ozone depleting and have minimal weight and space impacts on the vehicles. Any toxic gases formed during the fire extinguishing process must be at acceptable levels.

Technical Approach: Non-ozone depleting candidate for extinguishing agents will be studied for their ability to extinguish JP-8 fuel fires. The study will be conducted in a chamber whose interior volume is approximately that of a generic combat vehicle. A comparison of the amounts required to extinguish various size JP-8 fire will be made for different agents. Analyses of gases inside the chamber will be conducted to rank agents on bases of toxic gases produced during extinguishment.

Relationship to DoD Environmental Objectives: Removal of Halon 1301 from Army combat vehicle is a DoD requirement. Any replacement agent must be a non-ozone depleter. Identification of suitable replacement agents will contribute useful information to test programs for qualifying new agents on Army combat vehicles.

Relationship to Other Ongoing Work: The Navy and Air Force have active halon replacement programs. Several members of HARC (Halon Alternatives Research Corporation) have active programs in this area. Information gained will be shared with others interested in the halon replacement problem.

Tasks/Activities: Input from our 6.1 program, consultation with other DoD and private industry will be used to identify potential replacement agents for testing in a generic system. Agents will be ranked according to their ability to extinguish various sized JP-8 fuel fires. Analyses of gases produced during the extinguishment process will be carried out. Another ranking of agents will be made according to toxic gas production. An overall ranking of potentially useable agents will be made and the information disseminated to interested parties.

Technical Issues to Overcome: The halons are very efficient fire extinguishing agents because they contain bromine. But it is the bromine which causes the halons to have ozone depletion potential problems. Replacement agents will probably not contain bromine. Therefore, they may well be less efficient than the halons. This probably translates to extra volume of agents required for fire protection. It is very difficult to find any extra storage room on a fielded combat vehicle. An agent with a lower efficiency than halon may well produce more toxic gases during fire extinguishing scenarios due to longer time in the flame ozone. Toxic gases can be a major problem in crew compartments.

8. Expected Payoff:

Potential Users: Both DoD and private industry would welcome a non-ozone depleting, low cost, efficient fire extinguishing agent with acceptable toxic gases production. There is a potential payoff for all of DoD and the world in general.

Impact: The removal of halon from combat vehicles must be carried out independent of cost considerations. The identification of acceptable replacement agents at low cost would be very beneficial. The quicker the changeover from halon to a new agent in our combat vehicles, the better from an environmental point of view. There will be fewer accidental discharges of halon if it is removed quickly.

9. Milestones:

Identification and procurement of agents to be used in JP-8 fire tests - 6 months after award.
Testing for efficiency and toxic gas production for at least 3 agents - 12 months after award.
Testing for efficiency and toxic gas production for remaining agents - 24 months after award.
Tests of new agents which appear - 30 months after award.
Transfer of test result results and recommendations to TACOM, TECOM and other interested parties - 36 months after award.

10. Transition Plan:

Transfer: TECOM, which is responsible for the testing of TACOM's vehicles, will be kept informed continuously of our results in testing new agents. TECOM will be responsible for vehicle testing for the most promising agents. Member of HARC will be informed of our results through regular HARC technical committee meetings.

Coordination: TECOM, TACOM, the Navy and the Air Force will be continuously informed. The Navy and the Air Force will share all information with the Army to solve this common halon replacement problem.

11. Performers:

In-house work will be performed at the Army Research Laboratory/Weapons Technology Directorate, Aberdeen Proving Ground, MD. Involvement by Universities, a non-profit Research Institute and industry will be determined from an Army Research Office study of potential partners.

Coop Development Agreements: To be determined from an Army Research Office study.

12. Funding: ($K)

	FY94	FY95	FY96
IN-HOUSE	155	150	150
CONTRACT	295	350	350
TOTAL	450	500	500

13. Principal Investigator:

Dr. Anthony E. Finnerty
U.S. Army Research Laboratory
Weapons Technology Directorate
Aberdeen Proving Ground, MD
TEL: 410-278-6572
FAX: 410-278-8736

14. Keywords:

halons, fire extinguishment, JP-8 fuel fires, flame chemistry model, flame research, toxic gases, crew compartment fires

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Continuous Aqueous Cleaning to Eliminate ODC

3. **Agency:** Army

4. **Laboratory:** Rock Island Arsenal (RIA)/ARDEC

5. **Proposal ID:** #634

6. **Problem Statement:**

Typical metal parts painting operations require cleaning or degreasing immediately prior to the application of paint which utilize stratospheric ozone-depleting chemical (ODC) containing solvents. The adverse environmental impact Army material production and maintenance if alternatives are not implemented. An international agreement, federal environmental regulations, DoD directives, and Army Material Command regulations all mandate that research and development be performed to identify and implement ODC alternatives. Technology demonstration research is necessary to validate the implementation of specific technologies that have no adverse effects on the short and long term performance of military unique metal parts that are cleaned and painted. To date, the Army has not attempted to validate a continuous, in-line, aqueous-based cleaning system for such a use. This research effort will supplement prior Army research that has been conducted in the area of metal parts cleaning.

7. **Project Description:**

This effort will attempt to validate an aqueous-based cleaning system for degreasing metal parts at Rock Island Arsenal prior to the application of a chemical agent resistance coating (CARC). Currently, an ozone-depleting chemical solvent, 1,1,1-trichloroethane, is being used in a vapor degreaser to remove contaminant from metal parts prior to applying CARC paint during material maintenance procedures. Parts cleaned with this solvent are rendered completely dry and free from any cleaning agent residue, as required for proper paint adhesion. Biodegradable aqueous-based cleaners have been proven to work for batch type applications , but additional research focussing on continuous systems is needed.

The project is divided into three parts. The first part involves the selection of an aqueous-based cleaner that will adequately remove the contaminants from the different types of metals processed. To compliment the cleaner, use of the proper type of equipment is essential. Therefore, the second part of the project is to develop equipment specifications and a purchase description, including the appropriate waste water treatment system requirements. Since the parts cleaned will be subsequently painted, special difficulties exist with respect to adequate drying of the parts after the final rinsing operation. Lastly, the third part of the project is to select and install the most feasible alternative metal parts cleaning system.

8. **Expected Payoff:**

Successful implementation of this effort will eliminate the pollution and associated liabilities generated from fugitive solvent vapor emissions and hazardous waste resulting from spent

cleaning solvents. Industrial hygiene risks will also be reduce by eliminating the use of hazardous cleaning solvents. Ind addition, mission readiness will be preserved by eliminating the Army's dependence on these solvents, which because of their ozone-depletion potential, are being banned from future production and importation.

9. Milestones:

		Completion Dates
1.	Bench-scale test alternative cleaners	4/93*
2.	Develop equipment specifications	7/93*
3.	Provide specifications to vendors	10/93
4.	Technical review of proposals	1/94
5.	Equipment performance testing	7/94
6.	Vendor selection	10/94
7.	Equipment installation and testing	4/95
8.	Final report	7/95

* Completed

10. Transition Plan:

Once the use of continuous aqueous-based (pre-painting) metal parts cleaning technology has been validated for a particular Army us at Rock Island Arsenal, experimentation can be conducted to determine system operating parameters for other applications. Other military and commercial users with similar metal parts cleaning requirements will benefit from this research.

11. Funding: ($K)

	FY93	FY94	FY95	TOTAL
SERDP	60*	110	550	720

12. Performers:

This effort will be performed by the Advanced Technology Branch of the Science and Engineering Directorate at Rock Island Arsenal. Technical support will be provided by the Battlefield Automation and Technical Data Directorate of the Armament Research, Development and Engineering Center (ARDEC).

13. Principal Investigator:

Tera Hill
SMCRI-SEM-T
Rock Island Arsenal, IL 61299-5000
TEL: (309) 782-7860
FAX: (309) 782-7122

14. Keywords:

solvents, cleaning, degreasing, painting, trichlorethane, OD

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non Ozone Depleting Sealants for Ammunition Applications

3. **Agency:** Army

4. **Laboratory:** U.S. Army Armament, Research, Development, and Engineering Center (ARDEC)

5. **Proposal ID:** #674

6. **Problem Statement:**

Goal: The goal of this program is to eliminate and replace the currently used series of ozone depleting case mouth sealants, for small and medium caliber ammunition, with environmentally safe alternatives. These materials would also be applicable for threaded and fitted material components such as fuzes.

Background: Currently, the Army, Navy, Air Force, Special Forces, and other military organizations have mandated the elimination of Ozone Depleting Chemicals (ODC's). Unfortunately, most of the military's small and medium caliber ammunition, currently in the inventory, uses solvent rich, highly toxic, ozone depleting chemicals (1,1,1 trichloroethane, keytones, etc.). It is essential that these materials be replaced with solvent-free or solvent-safe case mouth sealants. This is necessary because the commercial equipment and practices currently available have been found to be relatively ineffective in controlling VOC emissions.

7. **Project Description:**

Technical Objective: This research program is aimed at investigating alternate solvent-free or solvent-safe case mouth sealants for military ammunition. This will be accomplished by evaluating state-of-the-art, commercially available non ozone depleting sealants.

Technical Approach: Efforts will be aimed at testing and documenting the compatibility, reliability, and durability of non-ozone depleting sealants that will also meet all of the ammunition acceptance requirements. Promising candidates then will be subjected to functional testing and characterization, as well as lot acceptance evaluation. Initial selection of commercial materials will be based on a study of mechanical, chemical, and physical property data as well as manufacturers recommendations.

Tasks:

- Document sealant properties relevant to ammunition applications
- Conduct compatibility and long term evaluations
- Conduct functional testing
- Evaluate on line application techniques
- Document data for technology transfer

Relationship to DoD/DOE Environmental Objectives: DoD/DOE has mandated the reduction/elimination of ozone depleting chemicals from military material.

Other Work: The reduction/elimination of ozone depleting chemicals is a relatively new requirement, and similar/prior R&D efforts in this field have not been found.

Technical risks are minimal for this proposed effort.

8. Expected Payoff:

A payoff is expected in several specific areas. First and foremost is that significant amounts of sealants with ozone depleting, toxic solvents, such as 1,1,1, trichloroethane, keytones, etc., will be eliminated; yielding a notable environmental benefit. As an example, the yearly usage of ODC sealants that would be eliminated at the Lake City Army Ammunition Plant is estimated at 2,000 gallons of 1,1,1 trichloroethane (5.56mm, 7.62mm, and .50 cal rounds) and 700 gallons of other assorted ODC solvents (20mm rounds). Economic benefits include reduced costs (elimination of toxic ODC environmental protection activities), increased production rates, reduced scrap ammunition (estimated at $2 million per year), and reduced lot rejection rate (which currently averages 6% per year. Other benefits include reduced ODC health/ safety problems, reduced misfires/hangfires, decreased damage to weapon systems/vehicles, and improved personnel safety.

9. Milestones:

1. Document sealant properties for military applications - Year 1
2. Conduct compatibility/long term evaluations - Years 1-3
3. Conduct functional testing - Years 2-3
4. Evaluate high rate on line application - Years 2-3
5. Document data for technology transfer - Years 1-3

10. Transition Plan:

Acceptable materials will be commercially produced sealants that are readily available for immediate use. Project R&D personnel will be working closely with users and producers to ensure that useful needed sealants are selected and are readily available to the production arena.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	250	250	250	750

12. Performers:

The Adhesives Section of the Armament Engineering Directorate, U. S. Army Armament Research, Development and Engineering Center will perform the study, working in close coordination with industrial manufacturers/suppliers and with other government organizations: Close Combat Armament Center (CCAC), ARDEC (all rounds); Olin Corp., Lake City Army Ammunition Plant (LCAAP) (5.56mm, 7.62mm, .50 cal, M50, GPU); Ballistic Services Office

(LCAAP) (test & evaluation); McAllister Army Depot (M90); Weapons System Laboratory Navy (M50); Hill Air Force Base (M50, M90, PGU); Elgin Air Force Base (M50, M90, PGU).

13. Principal Investigators:

Donald T. Rorabaugh and Dean Martinelli
SMCAR-AET-M
Building 183
Adhesives Section
ARDEC
Picatinny Arsenal, NJ 07806-5000
TEL: (201) 724-4482 / (201) 724-5333
FAX: (201) 724-2864

14. Keywords:

ozone depleting substances, TCE, case mouth sealants

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Replacement of Hydrochlorofluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs)

3. **Agency:** Army

4. **Laboratory:** U.S. Army Belvoir Research, Development, and Engineering Center

5. **Proposal ID:** #677

6. Problem Statement:

Goal: Evaluate HCFC-22 non-ozone depleting alternative refrigerants in existing military ECUs and develop optimized retrofit designs using the best of the refrigerant substitutes.

Background: An international treaty, the "Montreal Protocol on Substances that Deplete the Ozone Layer," and the Clean Air Act Amendment of 1990 require that the production and consumption of chlorofluorocarbons, hydrochlorofluorocarbons, halons, carbon tetrachloride, and methyl chloroform be phased out early in the 21st century. The Department of Defense procures significant quantities of ozone-depleting chemicals each year. The present inventory of ECUs within DoD represents approximately 125,000 pounds of ozone depleting chemicals.

Industry and Government agencies have been working to identify refrigerant replacements for HCFC-22. In 1991, the Air Conditioning and Refrigeration Institute (ARI) formed a Task Force to launch a cooperative research effort to identify alternatives to HCFC-22. Although the final results will not be published until July 1994 the preliminary results indicate that eight possible substitutes for HCFC-22 will be identified. ARI's role will be limited to providing basic thermophysical, material compatibility, and toxicological data to refrigeration manufacturers; "selecting the alternative fluid(s) most appropriate for a specific application and the designing of optimized equipment are tasks left to individual developers and manufacturers" (ARI quote). The Army therefore must ensure that its unique requirements and equipment are matched with the proper refrigerant.

Previously funded SERDP efforts: None

7. Project Description:

Technical Objective: Develop a knowledge of the performance of drop-in refrigerants to allow for the update of MIL-STD ECU technical data packages with non-ODS refrigerants.

Technical Approach: Select leading candidate HCFC-22 refrigerant replacements for testing based on ARI studies and computer analysis. Perform baseline performance tests on MIL-STD ECUs with HCFC-22. Convert to selected drop-in refrigerants and conduct performance tests at normal commercial rating points and at high temperatures required for military ECUs. Down-select to one or two refrigerants and conduct extended life tests to determine long term effects of drop-in refrigerants. Concurrently with ECU testing update existing software simulation code to reflect thermophysical properties being developed by the National Institute of Science and

Technology (NIST) and heat transfer properties being developed by the Electric Power Research Institute. The simulation software will be validated against the actual testing and used to optimize military ECU designs/component selection with the new refrigerants.

Tasks:

- Select leading replacement fluids for MIL-STD ECUs
- Update vapor cycle simulation code
  - thermophysics data
  - advanced heat transfer surface data
- Establish baseline performance profiles with HCFC-22
- Modify candidate ECUs based on ADEP material compatibility research
- Install new refrigerant and compatible lubricant
- Conduct reliability/ASHRAE-16 capacity tests
- Validate simulation model against test data
- Conduct component inspection and analysis
- Simulate and characterize performance across the family of military ECUs
- Identify deficiencies and determine corrective actions to retrofit military ECUs

Relationship to DoD/DOE Environmental Objectives: This program directly addresses the DoD directive to accelerate actions to phase out use of ODCs, by giving priority attention to revising specifications and requirements to eliminate the use of these chemicals (DoD directive, dated August 11, 1992, signed by Mr. Don Yockey, Under Secretary of Defense). This effort also supports the 1990 Clean Air Act Amendment and the Montreal Protocol international treaty.

Technical Risks: The risks are considered low to moderate that a refrigerant will be found that has suitable characteristics for use in military ECUs. Performance degradation of drop-in refrigerants may require system component engineering to compensate for degradation.

8. Expected Payoff:

Payoff will be reflected in the savings of not having to replace the existing inventory of approximately 26,000 Army ECUs worth $150 million.

9. Milestones:

Projected accomplishments during the execution year: Obtain data from NIST and EPRI and update existing vapor cycle simulation code. Review material compatibility studies and physical properties and determine best candidate refrigerant HCFC-22 replacements for military applications. Order military ECUs for testing and review technical data package for material compatibility with selected refrigerants.

Chart projected tasks/milestones throughout the life of the project (see enclosure 1)

10. Transition Plan:

Roadmap for transfer to the next stage through implementation: The subject proposal will result in a selection of a best HCFC-22 replacement for MIL-STD ECUs. It is envisioned that drawing and specification changes required to support the new refrigerant will be implemented through Engineering Change Proposals (ECPs) and Modification Work Orders (MWOs).

Coordination between performer and user: Coordination is being conducted with the user representative, i.e., the Ordnance Center and School, on improvements to the Army Environmental Control Unit family.

Industry ability to assume production: Through the ARI Alternative Refrigerant Evaluation Program (AREP) industry is working to develop manufacturing capabilities and practices to support each of the eight refrigerants comprising the replacement family for HCFC-22.

11. Funding: ($K)

	FY94	FY95	FY96	TOTAL
SERDP	250K	525K	150K	925
In-house Gov't	105K	250K	100K	455

12. Performers:

Department/Agency Laboratory: Work will be performed by the Environmental Equipment Development Team at the Belvoir Research, Development and Engineering Center.

Industry involvement: The Air-Conditioning and Refrigeration Institute is coordinating industrial involvement within the United States. ARI has established a Task Force Committee and a Technical Committee which have representatives from the leading refrigerant manufactures within the United States. International coordination is conducted through the European Committee of Manufactures of Refrigeration Equipment (CECOMAF) and the Japan Refrigeration and Air Conditioning Industry Association (JRAIA).

Planned cooperative development agreements: As part of ARI's coordination effort an automated database of industry and Government research and development has been established. All work performed under the subject proposal will be submitted for review and coordination to this technical database.

13. Principal Investigator:

Chris W. Bolton
U. S. Army Belvoir
Research Development and Engineering Center
Attn: SATBE-FED
Fort Belvoir, Virginia 22060-5606
TEL: (703) 704-1995
FAX: (703) 704-2005

14. Keywords:

HCFC-22, alternative refrigerants, hydrofluorocarbons, ozone depleting substances, environmental control units (ECUs)

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Advanced Streaming Agent

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory

5. **Proposal ID:** #158

6. **Problem Statement:**

Although extensive research has been conducted by both industry and the Department of Defense (DoD), a suitable replacement for Halon 1211 used in flightline and aircraft portable fire extinguishers has not been found/developed. Prior efforts to find a replacement concentrated on currently in-production chemicals and were directed at finding a chemical that had a low to zero ozone depletion potential (ODP), was non-corrosive, left little to no residue, had low toxicity, and had a fire suppressant effectiveness close to that of Halon 1211. Extensive research and testing efforts by the Air Force's Wright Laboratory (WL/FIVCF) identified perfluorohexane (C_6F_{14}) as the recommended candidate replacement agent for the DoD. Perfluorohexane, meets all performance requirements, but has a long atmospheric lifetime, which means it could contribute to global warming. Therefore, the US Environmental Protection Agency tentatively approved perfluorohexane for military fire fighting use only. Air Force Headquarters (AF/CE/LGM) subsequently decided not to recommend fielding of this chemical in view of this and possible future more stringent restrictions. As a result, WL/FIVCF has initiated a preliminary research effort to develop a second generation fire suppressant which will meet the original Halon 1211 replacement agent requirement as well as having a low to zero global warming potential (GWP). This proposal provides for continuation of this preliminary effort.

7. **Project Description:**

The prior research work identified several classes of chemical compounds not in commercial production that exhibit fire suppressant characteristics equal to or better than halons. The most promising of these include bromofluoroalkenes, fluoroiodocarbons, aromatic bromine-containing halocarbons, polar-substituent bromocarbons, and non-volatile precursors. The objective of this effort is to develop a "drop-in" clean, environmentally safe streaming fire suppressant to replace Halon 1211 used in flightline and aircraft portable fire extinguishers. The candidate compounds will be examined for their global environmental impact to insure that those that are filtered through to advanced testing have low/zero ODP and GWP. The major uncertainties at present are their toxicity and manufacturability. The primary focus in the initial screening of these compounds will be to perform preliminary toxicity evaluations. A manufacturing/synthesis assessment will be conducted in the initial evaluation to insure that the emerging candidates are able to be manufactured at reasonable cost. The best candidates to emerge from screening will be manufactured in a small pilot plant to create sufficient quantities for medium and large scale testing, materials compatibility testing, and validation testing. Coordination with manufacturers for technology transfer in the latter

stages of the program will be an important consideration for matching Air Force demand to private sector capacity. The Air Force is taking the lead in exploring this class of chemicals. Close coordination and collaboration with the Army, Navy, industry and academia is being exercised to avoid possible duplication and to take advantage of synergistic opportunities.

Tie to Tri-service Environmental Quality R&D Strategic Plan:

Pillar Thrust Area:	3.H
Requirements Category:	3.II.4.c
Work effort:	Tech Demo

8. Expected Payoff:

The successful completion of this research effort will provide the Air Force and other DoD components with a replacement for Halon 1211, a heavy ozone depleter. A Halon 1211-like agent is required for use in Air Force and other DoD component flightline and portable aircraft fire extinguishers due that agent's excellent fire suppression capability and zero residue and non-corrosive characteristics. These characteristics are essential for fighting aircraft engine and manned compartment fires. Due to the widespread use of Halon 1211 fire extinguishers in the civilian community, the agent developed in this research effort will also be of significant benefit to that sector.

9. Milestones:

1. Complete survey compounds/fire suppression mechanisms	03/94
2. Complete manufacturing /synthesis assessment	05/94
3. Complete global environmental impact assessment	09/94
4. Complete preliminary toxicity evaluations	12/94
5. Complete initial laboratory testing	03/95
6. Complete stability evaluations	09/95
7. Complete medium Scale Tests	03/96
8. Complete pilot plant studies: synthesis	09/96
9. Complete materials compatibility	12/96
10. Complete toxicity studies	01/97
11. Complete large scale testing	06/97
12. Complete operational validation	12/97

10. Transition Plan:

The effort will produce a streaming agent purchase specification and technical documentation covering materials compatibility, combustion products, and fire extinguisher performance tests results. These products will be transitioned to the Air Force Material Command, Aeronautical Systems Center (ASC/YOC) for the Engineering Manufacturing Development (EMD) phase. The EMD effort will, if necessary, develop and test any modifications to flightline and aircraft portable fire extinguishers to accept the new agent and will implement an agent change-out program. The same data will be provided to the Army, Navy, and industry for application, as appropriate. Industry has the capability to produce the chemical compounds of interest in laboratory quantities. It is believed that a cost effective volume production capability can be established for the selected compound(s). This should be confirmed by the manufacturabilty assessment to be conducted as part of the currently on-going effort.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	0	850	850	850	2550
USAF	600	0	0	0	600
TOTAL	600	850	850	850	3150

12. Performers:

This project is being managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall AFB, Florida. A SETA Subtask has been awarded to accomplish the first phase of the research effort, i.e., through initial laboratory testing. A task order contract and/or additional SETA Subtasks, as appropriate, will be used for the follow-on phases. The SETA contractor, Applied Research Associates, has subcontracted the initial research work to the New Mexico Engineering Research Institute. Preliminary toxicity efforts are being conducted by the Armstrong Laboratory (AL/OET). An expert panel will be established to conduct initial and periodic reviews of the technical approach; data collection procedures; interpretation of results; and environmental, regulatory, and safety issues that may have a impact on agent viability. Throughout the program , actions by standards making organizations involved in fire protection, including the Nation Fire Protection Association (NFPA), and by environmental regulatory agencies - in particular, the US Environmental Protection Agency - will be reviewed to ensure that agents developed are in full compliance with planned standards and regulations. Other players in the fire research arena that will be used or consulted include, but are not limited to, the University of Florida, chemicals manufacturers, and fire extinguishing equipment manufacturers. Close coordination, to include joint testing, will be maintained with the Army and Navy to ensure the selected agent meets their mission requirements.

13. Principal Investigator:

Dr. Charles J. Kibert
WL/FIVCF (Stop 37)
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
Tel: (904) 283-3745 DSN 523-3745
Fax: (904) 286-6763

14. Keywords:

Halon 1211, Fire suppression, Halocarbons, Bromocarbons, Fluoroiodocarbons, Bromofluoroalkenes

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Encapsulated Micron Aerosol Fire Suppression Technology

3. **Agency:** U.S. Air Force

4. **Laboratory:** Wright Laboratory (WL/FIVCF, Tyndall AFB, Florida)

5. **Proposal ID:** #113

6. **Problem Statement:**

This project seeks to develop and test a new fire suppression concept leveraged on Soviet aerosol technology for use in a wide variety of facility and aircraft protection roles. Halons, while powerful fire suppressants, cause ozone depletion and are being eliminated. Halon 1301 replacement candidates identified thus far are 2-3 times less effective than Halon 1301 in fire suppression efficiency. Known replacement agents would require major modifications to piping, nozzles, and other components of the delivery systems. Suitable replacements resulting from existing programs and technologies are not available or projected to be available in the near term. A class of environmentally safe agents that can fulfill some of these fire suppression roles is badly needed and required to maintain the operational readiness and capability of the Air Force. Encapsulated Micron Aerosol Agents (EMAA) may provide the Air Force with an environmentally and occupationally safe agent that has 6 times the fire suppression capability of Halon 1301 by weight. It requires no piping or pressure cylinders and will be a fraction of the cost of Halon 1301 in installation and life cycle costs. It also allows delivery strategies other than total flood and can be placed locally in high fire risk locations within a facility. FY94 SERDP funding will be used to continue a program initiated with FY93 SERDP and USAF funds. FY94 funding will be split 50-50 between applied research and technology demonstration.

7. **Project Description:**

Various EMAA formulations will be tested for fire suppression efficiency, materials compatibility, storage stability and lifetime, packaging, toxicity, electrical conductivity, corrosion, and combustion products. The results of these analyses will be utilized in the engineering of delivery systems for both total-flood and local fire suppression strategies. Several delivery packages and methods containing both non-electrical and electrical initiation will be designed, fabricated, and tested to determine the best practical methods for delivering fire suppression aerosols. Ultimately, large scale testing against scenario fires will be conducted to determine the final configuration of EMAA delivery systems. A CRADA with Spectrex, Inc. will result in the basic aerosol compositions and chemistry being assessed. Applications for EMAA will center around local delivery systems that can be used without the need to resort to a total flooding of the space being protected. Possible strategies include placing an EMAA device directly in equipment that is a potential source of fire. The risks of this program are moderate. The major difficulties are the corrosion potential of the EMAA solids in a humid atmosphere, toxicological effects of lung penetration of the micron and submicron sized particles, and the handling of high temperatures and energy developed in

the creation of the aerosol. The technical program addresses each of these areas and provides for detailed analysis of each of these potential problem areas.

Tie to Tri-service Environmental Quality R&D Strategic Plan
Pillar Thrust Area: 3.H
Requirements Category: II.4
Work effort: Tech Demo

8. Expected Payoff:

The successful development of pyrotechnically generated aerosols as envisioned in this program will provide the Air Force with a badly needed option in the drive to replace Halon 1301 with non-ozone depleting fire suppressants. In addition to removing the threat of an environmentally unacceptable chemical, EMAA actually provides superior performance on a weight and volume basis. The result will be new applications such as fire protection systems that can be easily built into deployable shelters, hand thrown and remotely launched devices that can be used to provide "first-aid" to begin the process of extinguishment, and the potential to protect large fuel storage tanks from destruction via compact fire suppression systems. The Air Force also stands to benefit economically from the development of EMAA applications because the provisions of the CRADA call for royalties to be paid to the Air Force for products created and sold as a result of the Air Force research and development investment.

9. Milestones:

1.	Selection of Aerosol Formulations	03/94
2.	Particle Characterization	04/94
3.	Extinguishment Mechanisms	05/94
4.	Completion of Corrosion Studies	06/94
5.	Thermal Characterization	07/94
6.	Ignition Methods	08/94
7.	Energy Absorption Methods	09/94
8.	Fire Suppression Effectiveness	09/94
9.	Toxicity Testing	01/95
10.	Stability Testing	03/95
11.	Hand Thrown Device Testing	05/95
12.	Remote Launch Device Testing	07/95
13.	Medium Scale Facility Tests	08/95
14.	Delivery System Design/Testing	01/96
15.	Large Scale Tests	08/96
16.	Final Report	10/96

10. Transition Plan:

A CRADA merges the efforts of Air Force laboratories with Spectrex, Inc. to produce a powerful yet low cost fire protection system. Provisions in the CRADA create devices that are suitable for Air Force applications and create a licensing scheme that will allow multiple source commercialization of the end products. The CRADA requires that the Air Force receive royalties that, if the project is fully successful, will more than recover the development investment of the Air Force.

11. Funding: ($K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	650	630	630	735	2645
USAF	200	0	0	0	200
TOTAL	850	630	630	735	2845

12. Performers:

This project will be managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall Air Force Base, Florida. Extensive coordination and cooperation will be a accomplished with Spectrex, Inc. Spectrex will handle issues of agent composition whereas WL/FIVCF is responsible for technical issues such as corrosion assessment, initial toxicological assessment, particle size measurements, thermal characterization, thermal absorption studies, calorimetry, and applications engineering. Several contractors will be utilized to accomplish the tasks under this effort to include Applied Research Associates (ARA), the New Mexico Engineering Research Institute (NMERI), the University of Massachusetts (Lowell), and the University of Florida. Extensive coordination will be conducted with the Army, Navy, and the FAA due to their interest in possibly utilizing this technology for their own purposes.

13. Principal Investigator:

Dr. Charles J. Kibert
WL/FIVCF (Stop 37)
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323
Tel: (904) 283-3745
DSN: 523-3745
Fax: (904) 286-6763

14. Keywords:

Halon 1301, Encapsulated Micron Aerosol, Fire suppressants, Ozone depleting substances, HCFCs, Aerosols

SERDP FY94 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention

2. **Title:** Non-Ozone Depleting Refrigerants for Navy Chillers

3. **Agency:** Environmental Protection Agency (EPA)

4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)

5. **Proposal ID:** #309

6. **Problem Statement:**

The Navy currently has approximately 900 shipboard chillers using CFC-114 refrigerant for purposes of vital equipment cooling and comfort air-conditioning. By law, production of CFC-114 must cease by December 31, 1995. The Navy must, therefore, find a suitable alternative refrigerant to retrofit all of its CFC-114 chillers as the supply of CFC-114 dwindles or convert the entire fleet to entirely different cooling plants. Retrofitting existing chillers instead of replacing these units would save the Navy in excess of $500 million. Projected unavailability of CFC-114 requires that the Navy commence retrofitting the fleet in the 1997 to 1998 time frame.

The EPA (Environmental Protection Agency) has been researching potential CFC-114 alternatives since 1988. Through this program, two non-ozone depleting, low global warming candidate alternatives (i.e., HFC-236ea and HFC-236fa) have emerged which appear to be especially promising. The Navy, through its own evaluation of several possible alternatives, has also concluded that HFC-236ea and HFC-236fa are among the most viable retrofit candidates. However, in order to meet the stringent retrofit deadlines, further evaluations of HFC-236ea and HFC-236fa must be completed prior to 1998. Toxicity testing of the chemicals is now recognized as that element of the development program which requires the greatest time to complete and which, therefore, defines the critical path to success. Additionally, further laboratory performance and materials evaluations of the chemicals are required to identify which of the two candidates is superior.

7. **Project Description:**

In anticipation of meeting the Navy's retrofit needs, the EPA requested and received FY91, FY92, and FY93 SERDP funds for acquisition and laboratory evaluation of HFC-236ea. Work is progressing satisfactorily in concert with the Navy's performance testing of both HFC-236ea and HFC-236fa in a 125-ton chiller of the type used on ships. This proposal is to continue and expand the evaluations of both chemicals along a parallel path until such time as one chemical can be clearly identified as superior to the other. When a preference for one of the chemicals is decided, further work will concentrate on the preferred alternative.

Completion of toxicity testing sufficient to enable the Navy to safely commence retrofit of shipboard chillers with the selected alternative refrigerant will be the main thrust of the proposed project. Initial acute inhalation toxicity tests such as determination of the LC_{50}, cardiac sensitivity threshold, and developmental toxicity are being conducted for HFC-236ea

with FY92 SERDP funds. FY93 SERDP funds are being utilized for determination of the genetic toxicity and 90-day subchronic inhalation toxicity of HFC-236ea.

The proposed 4-year project would complete genetic toxicity and 90-day subchronic inhalation toxicity tests for HFC-236fa and complete all required toxicological evaluations for the one preferred chemical, including evaluations imposed by the Navy as regards use of the chemical in confined spaces such as submarines.

Requested FY94-FY97 SERDP funds will also be used to procure quantities of HFC-236ea and HFC-236fa needed for the toxicity testing and for laboratory performance investigations which have been planned by the Navy. The Navy has recently established a laboratory facility and installed seven shipboard-type air conditioning plants for performance investigations of CFC-114 alternatives. These air-conditioning plants are the same designs which are currently installed on the Navy's most sophisticated aircraft carriers, surface combatants, and submarines. The Navy also has developed plans to procure 6 additional shipboard-type air-conditioning plants for a second phase of laboratory performance investigations. It has been estimated that up to 10,000 pounds of each chemical (HFC-236ea and HFC-236fa) will be required for the toxicity and performance investigations.

Engineering materials and lubricants compatible with the alternative refrigerants will be identified via AEERL in-house laboratory tests for use in the Navy's refrigerant performance investigations. Expansion of the thermophysical property database and determination of the heat transfer coefficients for HFC-236fa will also be accomplished with the requested FY94-97 funds.

This work directly supports the goals of Pillar 3 (Pollution Prevention) in the Tri-Source Research Plan which has a goal to eliminate the use of ODS (ozone-depleting substances) as soon as possible. Specifically, the project supports work under Thrust 3F to identify safe, affordable chemical substitutes for ODS refrigerants.

8. Expected Payoff:

Building upon the success of previous work, it appears very likely that HFC-236ea or HFC-236fa will be selected to replace CFC-114 in Navy shipboard chillers. This would enable the Navy to quickly eliminate the use of CFC-114 without incurring the major expense of converting all existing chillers to new equipment. Once implemented by the Navy, it is anticipated that additional uses of HFC-236ea or HFC-236fa would be identified in the private sector to further eliminate the Nation's dependence on ODS's.

9. Milestones:

1. Procure initial quantities of HFC-236ea & HFC-236fa	11/94
2. Identify engineering materials and optimized lubricants	12/94
3. Complete HFC-236fa subchronic and genetic toxicity tests	6/95
4. Procure additional chemical quantities	7/96
5. Complete balance of toxicity tests for preferred chemical	9/97

10. Transition Plan:

Toxicity testing must be completed prior to commercialization of any chemical. Results of such tests will be reported to the Navy and chemical producers to allow timely decisions to be made regarding selection of preferred retrofit chemical, any equipment design or construction modifications, and commercialization. Every attempt will be made to meet the retrofit deadlines set by the Navy.

11. Funding: ($K)

	FY91	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	500	500	300	1000	1750	750	500	5300
EPA	50	50	150*	50*	0	0	0	300
TOTAL	550*	550	450	1050	1750	750	500	5600

* Most of these funds were for performance related activities not toxicity.

12. Performers:

Primary: EPA/AEERL with contracts to toxicity testing laboratories and chemical suppliers.

Other: Naval Medical Research Institute, Robert Carpenter
Naval Sea Systems Command, Joel Krinsky

13. Principal Investigator:

William J. Rhodes (Overall Coordinator)
US Environmental Protection Agency
AEERL, Mail Drop 62B
Research Triangle Park, NC 27711
Phone: (919) 541-2853
Fax: (919) 541-7885

14. Keywords:

Refrigerant, Chillers, Ships, Stratospheric Ozone, CFC-114, toxicity

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